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Col. = Colorimetric, heterometric, photometric and spectrophotometric analysis — colorimétrie, hétérométrie, photométrie et spectrophotométrie — heterometrische, kolorimetrische, photometrische und spektrophotometrische Analyse
El. = Electrolytic analysis, electrolysis — dosage électrolytique, électrolyse — elektrolytische Analyse, Elektrolyse
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STRUCTURE AND BEHAVIOR OF ORGANIC ANALYTICAL REAGENTS

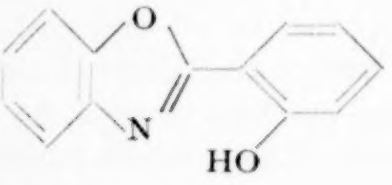
IV. CHELATES OF 2-(*o*-HYDROXYPHENYL)-BENZOXAZOLE, 2-(*o*-HYDROXYPHENYL)-BENZOTHIAZOLE AND 2-(*o*-HYDROXYPHENYL)-BENZOTHIAZOLINE.*,**

by

ROBERT G. CHARLES AND HENRY FREISER

Contribution 881 of the Department of Chemistry, University of Pittsburgh (U.S.A.)

A number of organic compounds are known which contain essentially the same reactive groups as the important analytical reagent 8-hydroxyquinoline, but so arranged as to give six-membered rings when chelating with metal ions. In Paper III[1] of this series, JOHNSTON AND FREISER obtained results which seemed to indicate that reagents of this type form metal chelates of lower stability than do those reagents which form five-membered ring chelates. In view of these results it was thought desirable to extend the study of six-membered ring chelate formers. 2-(*o*-Hydroxyphenyl)-benzoxazole (I) was chosen for study because preliminary work had shown that this reagent reacts readily with a number of metal ions, and also because, unlike certain analogous reagents such as the Schiff bases derived from salicylaldehyde, it is known to be moderately stable in acid solution[2]. The study was extended to 2-(*o*-hydroxyphenyl)-benzothiazole (II) in order to determine the effect of substituting the larger sulfur atom for the oxazole oxygen. A study of the reaction between *o*-aminobenzenethiol and salicylaldehyde, which has been thought to give (II)[5,4] has been shown to actually give the corresponding thiazoline[5] (III). This substance was found to be itself a chelating agent and was included in the present work for purposes of comparison.



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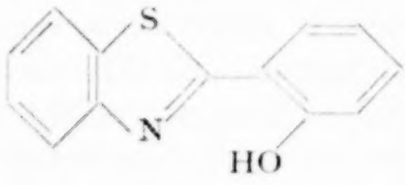

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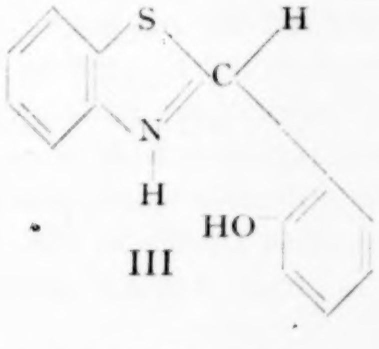

III

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* For paper III, see reference 1.

** Abstracted from the thesis submitted by ROBERT G. CHARLES in partial fulfilment of the requirements for the Ph. D. degree in Chemistry, August 1952.

EXPERIMENTAL

Materials. The purification of the 1,4-dioxane and the preparation and standardization of aqueous metal perchlorate solutions and of standard aqueous sodium hydroxide and aqueous perchloric acid have been previously described[6].

Metal ion solutions for qualitative tests, containing about 50 milligrams metal ion per milliliter, were prepared from reagent grade nitrates and distilled water.

2-(*o*-Hydroxyphenyl)-benzoxazole was prepared from *o*-aminophenol and salicylamide[2]. It was recrystallized three times from ethyl alcohol-water mixtures and dried in a vacuum desiccator. M. p. 126-127° C (corr.).

2-(*o*-Hydroxyphenyl)-benzothiazole was prepared in an analogous manner from *o*-aminobenzenethiol and salicylamide[5]. It was vacuum-distilled, recrystallized several times from ethyl alcohol-water mixtures, and dried in a vacuum desiccator. M. p. 132-133° C (corr.).

2-(*o*-Hydroxyphenyl)-benzothiazoline was prepared from *o*-aminobenzenethiol and salicylaldehyde[5]. The compound was recrystallized from ethyl alcohol-water and dried in vacuo. M. p. 136-137° C (corr.) with preheating to 130° C.

Stability measurements. Measurements of the stability of the chelates formed by three reagents described in this paper were carried out in 50% by volume 1,4-dioxane, 50% water by the modified Calvin-Bjerrum titration procedure described in paper I of this series[6]. Since some measurements were performed at 40° C, the response of the glass electrode in the 50% dioxane, 50% water medium was calibrated by titrating perchloric acid with sodium hydroxide under essentially the same conditions as those used for the stability measurements. It was assumed that the true hydrogen ion concentration at each point along the titration curve was equal to the concentration of unneutralized perchloric acid present at that point. The factor $C_{H^+} = \dfrac{[H^+]\ \text{calculated}}{[H^+]\text{observed}}$ was found to be equal to 0.73 ± 0.02 at 40° C and did not vary with pH over the acid portion of the curve or with ionic strength within the range employed. This factor was used to correct all pH values used in the stability calculations at 40° C. The corresponding value of C_{H^+} at 25° C was found to be 0.85 ± 0.02, which is close enough to 1.00 to be neglected for many purposes. It nevertheless was applied to all observed pH values at 25° C, used in the calculations. Although these corrections are based on observations made in acid solutions, the results were assumed to apply to the basic region as well. Since the sodium ion concentrations of the titration mixtures are uniformly small, which in turn results in a vanishingly small sodium error of the glass electrode, this assumption was considered proper.

Because of space restrictions the titration data are not included here *.

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* Complete tables of experimental data are included in reference 7.

Table I summarizes the values of the dissociation constants of the reagents determined by the previously described titration method[6] while Table II contains the stability constants of the chelates.

TABLE I

SUMMARY OF ACID DISSOCIATION CONSTANTS

	pK_{NH}	pK_{OH}	temperature (°C)
2-(*o*-Hydroxyphenyl)-benzoxazole	<2	11.57	24.9
	<2	11.37	39.5
2-(*o*-Hydroxyphenyl)-benzothiazole	<2	10.37	39.6
2-(*o*-Hydroxyphenyl)-	<2	10.22	25.0
*8-Hydroxyquinoline	3.97	11.54	25.0

* Data of W. D. JOHNSTON[1] included for comparison.

TABLE II

2-(*o*-Hydroxyphenyl)-benzoxazole	Excess reagent	log K_1	log K_2	log K_{av}	Temperature (°C)
Ni (II)	2-fold	8.60	7.74**	8.17	24.9
	4-fold	8.37	7.25**	7.81	39.5
Pb (II)	2-fold	7.7	6.1	7.3 6.9**	25.6
Mg (II)	4-fold	4.96	4.12	4.49 4.54**	39.7
2-(*o*-Hydroxyphenyl)-benzothiazole					
Ni (II)	5-fold	5.61	4.82	5.21 5.22**	39.6
Mg (II)	4-fold	3.06	—	—	39.6
2-(*o*-Hydroxyphenyl)-benzothiazoline					
Ni (II)	2-fold	6.59	5.36	5.96 5.98**	25.0
Co (II)	2-fold	9.80**	8.48	9.14	25.0
Fe (II)	2-fold	9.1	6.9	7.5 8.0**	25.0
Mn (II)	2-fold	5.88	4.56**	5.22	25.0
Zn (II)	2-fold	8.01	5.87	7.6 6.94	25.0
Pb (II)	2-fold	7.5	6.2	6.5 6.9**	25.0
La (III)	1.2-fold	7.30	6.08	(log K_3 = 5.44)	25.0

** refers to the calculation of the value so designated from the other two constants listed rather than by direct observation of the $\bar{n}$ - pR curve[6,7].

Reactions with metal ions

Qualitative precipitation tests with a number of metal ions were performed with each of the three reagents under several sets of experimental conditions.

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These tests were complicated by the insolubility of the reagents in water. The following general procedure, however, gave satisfactory results. Two to three milliliters of a saturated solution of the reagent in hot 50% ethyl alcohol-water was added to a nearly boiling mixture of two milliliters ethyl alcohol, two milliliters of the appropriate aqueous buffer solution, and sufficient metal ion to make the metal ion concentration of the final solution 0.5 to 1 milligram per milliliter. Solutions were observed immediately and also upon cooling. Where necessary, blank tests were also performed in the absence of reagent. The three buffers employed were the acetic acid-acetate buffer "A", the ammonia-tartrate buffer "B", and the sodium hydroxide-tartrate buffer "C", described by IRVING, BUTLER AND RING[8]. Tests in the presence of NH_4OH, only, were performed as above but without buffer and with sufficient $2N$ NH_4OH to make the final solution slightly ammoniacal. Metal ions employed in the tests were Cu(II), Ag(I), Ca(II), Sr(II), Ba(II), Mg(II), Zn(II), Cd(II), Hg(II), Al(III), Pb(II), As(III), Bi(III), Cr(III), Mn(II), Fe(III), Co(II), Ni(II). Metal ions giving positive precipitation tests with each reagent are given below.

2-(o-Hydroxyphenyl)-benzoxazole

Buffer "A": Cu(II), Fe(III)*, Co(II), Ni(II)
NH : Cu(II), Ca(II), Sr(II)*, Ba(II)*, Mg(II), Cd(II), Pb(II), Mn(II), Co(II), Ni(II)
Buffer "A": Cu(II), Co(II), Ni(II)
Buffer "C": Cu(II), Ca(II)*, Sr(II)*, Cd(II), Co(II)

2-(o-Hydroxyphenyl)-benzothiazole

Buffer "A": Cu(II); NH_3: Cu(II), Cd(II), Pb(II), Co(II), Ni(II)
Buffer "B": none
Buffer "C": Cd(II)

2-(o-Hydroxyphenyl)-benzothiazoline

Buffer "A": Cu(II), Ag(I), Zn(II), Cd(II), Hg(II), Pb(II)*, As(III)*, Bi(III), Cr(III), Fe(III), Co(II), Ni(II)
Buffer "B": Cu(II), Ag(I), Ba(II)*, Zn(II), Cd(II), Hg(II), Al(III), Pb(II), As(III), Bi(III), Cr(III), Fe(III), Co(II), Ni(II)
Buffer "C": Cu(II)**, Ag(I)*, Ca(II)*, Ba(II)*, Cd(II), Hg(II), Co(II)**, Ni(II)**

The colors of the precipitated salts of 2-(*o*-hydroxyphenyl)-benzoxazole are Cu(II), light brown; Ni(II), greenish yellow; Co(II), yellow; Zn(II), flesh colored; Pb(II), yellow; Cd, light yellow; Mn(II), white; Ca, pinkish white; Sr, white; Ba, white; Fe(III), dark red; Mg, white. The colors of the chelates of 2-(*o*-hydroxyphenyl)-benzothiazole are Cu(II), light brownish yellow changing to dark brown on heating; Cd(II), light yellow; Pb(II), yellow; Co(II), greenish yellow; Ni(II), bright yellow. The colors of the 2-(*o*-hydroxyphenyl)-benzothiazoline chelates are Cu(II), dark brown; Ag(I), orange, changing to white on heating; Co(II), dark red brown; Ni(II), reddish brown; Hg(II), yellow; Bi(III), orange; Fe(III), brownish black; Cd, bright yellow; Zn, bright yellow; As(III), yellow; Al, yellow; Cr(III), light yellow; Pb(II), bright orange.

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* Doubtful test or obviously incomplete precipitation
** Color change but no precipitate

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A number of the metal chelates of 2-(*o*-hydroxyphenyl)-benzoxazole were prepared and isolated in order to study some of their properties and also in order to test the applicability of the reagent as a precipitating agent for metal ions. With the exception of the copper salt, the chelates were prepared as follows. To 50 milliliters of standard aqueous $0.01M$ metal perchlorate solution were added 100 milliliters of distilled water, and the solution heated to 60° C. A solution of the reagent was prepared by dissolving one gram in 100 milliliters of ethyl alcohol. Twenty-five milliliters (a small excess) of the reagent solution was added slowly, with stirring, to the hot test solution, followed by the dropwise addition of sufficient $2M$ NH_4OH to make the solution definitely basic to litmus. The mixture was allowed to cool to room temperature and was filtered through a sintered glass crucible (medium porosity). Excess reagent was removed by washing the precipitate with several portions of 50% v/v ethyl alcohol-water (room temperature) to which a drop or two of dilute NH_4OH was added. The reagent is fairly soluble in this mixture while all the complexes described below appear to be quite insoluble. The washed precipitates were dried to constant weight at 130° C. All the chelates examined are hydrated as precipitated and lose water only slowly below 130° C.

The preparation of the Cu salt differed only in that 0.6 gram of sodium acetate was added instead of the NH_4OH. Composition of the precipitates was established by comparing the weights of the dried complexes with the theoretical values, and by nitrogen analysis. The results are summarized in Table III. Precipitation in all cases was found to be quantitative. In all cases the composition of the chelates corresponds to two organic chelating anions per metal atom.

In addition to the chelates listed in Table III, preliminary work has shown that the Mg(II), and Mn(II) salts are also precipitated quantitatively. However, the conditions described above are not applicable to these since the Mn(II) salt decomposes at 130° C and the Mg(II) salt is slightly soluble in 50% alcohol.

Since 2-(*o*-hydroxyphenyl)-benzoxazole, itself, fluoresces brightly under ultraviolet light, it was thought of interest to examine the chelates of this reagent under ultraviolet radiation. The following observations were made on the salts dried at 130° C: Cu(II), no fluorescence; Pb(II), green fluorescence; Ni(II), no fluorescence; Zn(II), bright blue fluorescence; Co(II), no fluorescence. The dried manganese and magnesium chelates were also examined: Mn(II), no fluorescence; Mg, bright blue fluorescence.

The Cu(II), Ni(II), Zn(II), and Co(II) chelates of 2-(*o*-hydroxyphenyl)-benzoxazole showed no evidence of melting or decomposition at 300° C, the highest

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TABLE III

METAL CHELATES OF 2-(*o*-HYDROXYPHENYL)-BENZOXAZOLE

Chelate	Weight of precipitate Calculated (grams)	Found	Per cent. N Calculated	Found
$Cu(C_{13}H_8NO_2)_2$	0.2318	0.2330 0.2319	5.79	5.92
$Ni(C_{13}H_8NO_2)_2$	0.2360	0.2349 0.2358	5.85	6.25
*$Co(C_{13}H_8NO_2)_2$	0.2381	0.2353	5.44	6.07
$Zn(C_{13}H_8NO_2)_2$	0.2272	0.2305 0.2299	5.77	5.90
$Pb(C_{13}H_8NO_2)_2$	0.3179	0.3142 0.3140	4.46	4.40

* Calculated for $Co(C_{13}H_8NO_2)_2$: C, 65.14; H, 3.36
Found: C, 64.58; H, 3.16

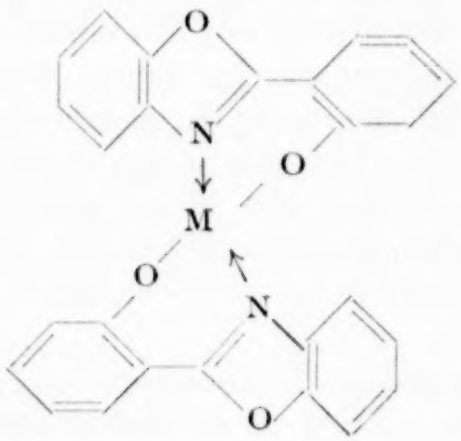
temperature tried. The Pb(II) salt began to decompose at about 280° C, but did not melt at 300° C.

The Cu(II), Pb(II), Ni(II), Zn(II), and Co(II) salts of 2-(*o*-hydroxyphenyl)-benzoxazole only slightly soluble in chloroform, very slightly soluble in benzene, and insoluble in absolute ethyl alcohol.

DISCUSSION OF RESULTS

The acid dissociation constant K_{OH} of 2-(*o*-hydroxyphenyl)-benzoxazole is nearly identical with that of 8-hydroxyquinoline[1] but significantly less than that found for 2-(*o*-hydroxyphenyl)-quinoline[1]. The oxazole reagent, unlike 8-hydroxyquinoline[1], has no measurable basicity (K too large to be determined by our method). It does, however, resemble 2-(*o*-hydroxyphenyl)-quinoline in this respect.

In all the stability titrations with divalent metal ions, two hydrogen ions were released per metal ion, corresponding to the expected structure of the complexes:



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where Me represents the metal atom. Additional proof of this structure is provided by the composition of the solid salts (Table III). This structure is closely analogous to that of 8-hydroxyquinoline chelates with the major difference that 8-hydroxyquinoline forms five-membered rings with the metal ion rather than six. It is therefore profitable to compare the stabilities of the chelates of these two compounds. The complexes of 2-(*o*-hydroxyphenyl)-benzoxazole were found to be be of much lower stability than the corresponding 8-hydroxyquinoline chelates[1], but of somewhat higher stability than the *o*-aminophenol chelates described in Paper II of this series[9]. Part of the difference in stability of the chelates of the oxazole and of 8-hydroxyquinoline is undoubtedly due to the lower nitrogen basicity of the former since the lower electron density about the nitrogen should result in weaker bonds being formed with metal ions. The difference in stability appears too great, however, to be due entirely to this cause. Steric considerations, that is, the greater difficulty of fitting the oxazole molecules about the metal ion, may be responsible for the rest of the decrease. It is significant, in this regard, that, with the exception of Fe(III) no precipitation reactions of the oxazole with trivalent ions were observed, indicating the difficulty of fitting three reagent anions about a trivalent metal ion.

The low solubilities of the complexes of 2-(*o*-hydroxyphenyl)-benzoxazole interfered with the determination of stability constants except in a few cases. However, the titration data obtained for the others were sufficient to establish the probable relative stability order of these complexes. The order found was Cu(II)>Co(II)>Ni(II)>Zn(II)>Pb(II)>Mg(II). With the exception of the apparent reversal of order in the case of Co and Ni this is similar to what has been found for 8-hydroxyquinoline[1].

Experimental difficulties restricted the study of the chelates of 2-(*o*-hydroxyphenyl-)benzothiazole to those of the two metals Ni(II) and Mg(II). Because of the rather low solubility of the chelating reagent, all measurements were made at 40° C rather than the usual 25° C. It will be noted that the thiazole is a somewhat stronger acid than the corresponding oxazole and like the oxazole has no measureable basicity. In the case of both metals studied with the thiazole, the complexes are significantly less stable than the corresponding oxazole complexes. Insufficient data were obtained to evaluate the order of decreasing stability for other metals. The decreased stability of the thiazole complexes relative to those of the oxazole is to be expected because of the higher acidity of the former compound[10] although this fact is probably insufficient to explain the entire decrease in stability. The complexes of 2-(*o*-hydroxyphenyl)-benzothiazole presumably have the same structure as that shown for the corresponding oxazole chelates above, although the stability titrations occurred at too high a pH to definitely establish the release of two hydrogen ions per metal ion.

It is interesting to compare the oxazole and thiazole with 2-(*o*-hydroxyphenyl)-

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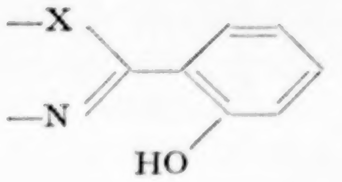
quinoline[1]. All of these compounds can be represented as having the following grouping:



where X is O with the oxazole, S with the thiazole and C=C with the quinoline compound. It appears that as the group X is increased in size, the stability of the complexes of the reagent decreases. A possible explanation for this would seem to be that, as the size of X is changed, the distance from the hydroxyl oxygen to the tertiary nitrogen changes, from an optimum value with the oxazole, to a value with the quinoline compound so unfavorable as to prevent chelate formation. It should be mentioned that while the higher acidity of the thiazole compound, with respect to the oxazole, can account in part for the decreased stability of the thiazole complexes, the same explanation cannot be advanced to explain the still lower stability of the chelates of 2-(*o*-hydroxyphenyl)-quinoline, since the latter is a much weaker acid than either the thiazole or the oxazole[1].

Stability measurements with 2-(*o*-hydroxyphenyl)-benzothiazoline (III) revealed a number of interesting facts. Like the oxazole and thiazole, the thiazoline has no measurable basicity. It will be noted that the acid dissociation constant of the thiazoline and that of the thiazole are of comparable size.

For the one metal, Ni(II), where data were obtained for both the thiazole and thiazoline, the complex with the thiazoline was found to be significantly more stable. It is possible that the greater freedom of motion of the thiazoline molecule may better adapt it to the spatial requirements of the metal ions.

The relative stability order of the metal complexes of the thiazoline is unusual. For the divalent metals the order seems to be Cu(II) > Co(II) > Fe(II) > Zn(II) > Pb(II) > Ni(II) > Mn(II). Nickel, particularly, seems to be displaced from its usual position in the order. This difference may be associated with steric interference imposed by the hydrogen bonded to the tertiary nitrogen. Additional studies on the complexes of the thiazoline, using other methods, would be desirable, to clarify the behavior of these interesting chelates.

In all the divalent metal ion-thiazoline titrations two hydrogen ions were released per metal ion, indicating a structure for the chelates similar to those of the oxazole complexes above. Three hydrogens per metal ion were released for La(III).

It is of interest to compare the qualitative behavior with metal ions of 2-(*o*-hydroxyphenyl)-benzoxazole, 2-(*o*-hydroxyphenyl)-benzothiazole, and 2-(*o*-hydroxyphenyl)-benzothiazoline. It will be noted that the reactions of the oxazole somewhat resemble those of 8-hydroxyquinoline[11], with the notable exception that the oxazole is more selective; that is, it reacts with a smaller number of metal ions under comparable conditions. This latter fact is in agreement with the lower stabilities found for the oxazole complexes in comparison with those of 8-hydroxyquinoline. Of particular interest is the lack of reactivity with trivalent ions, already mentioned.

The behavior of the oxazole in NaOH-tartrate solution is striking. Under these conditions only Cu(II), Co(II), and Cd(II) precipitate appreciably. Since Cu(II) and Co(II) also precipitate at lower pH values, and can thus be removed, it might be expected that the oxazole could be used as a highly selective precipitating agent for cadmium. This high degree of selectivity for cadmium, discovered in the present work, has since been applied by J. L. WALTER of this department, who found that the reagent can indeed be made nearly specific for cadmium[12].

A comparison of the qualitative reactions of 2-(*o*-hydroxyphenyl)-benzoxazole shows that a number of other interesting separations appear possible. The selective nature of the reagent, together with the favorable gravimetric factors associated with the precipitates, appears to make the oxazole potentially more useful than 8-hydroxyquinoline for certain determinations.

The qualitative reactions of metal ions with 2-(*o*-hydroxyphenyl)-benzothiazole resemble those of the oxazole, except that even greater selectivity is shown by the thiazole, in agreement with the lower stability of these complexes compared with those of the oxazole. The fact that apparently only cadmium of the metals tested is precipitated in the NaOH-tartrate buffer, indicates that the thiazole may be an even more selective reagent for cadmium than is the oxazole.

The precipitation of cadmium by the thiazole in the presence of copper is reminiscent of a similar separation by the use of hydrogen sulfide in a cyanide medium. In both cases the copper forms a more insoluble salt with the precipitating agent than does cadmium. The presence of masking agent with which copper forms a much more stable complex than does cadmium prevents the precipitation of the copper but not the precipitation of cadmium. This combination of chelating agent and a soluble complexing agent would seem to offer great promise for effecting interesting separations by increasing the effective selectivity of the reagent.

The qualitative reactions with metal ions of 2-(hydroxyphenyl)-benzothiazoline are entirely different from either those of the thiazole or oxazole. The thiazoline reacts with most of the common metal ions including the trivalents. This difference in selectivity is difficult to explain. Part of the difference is probably due to the increased stability of the complexes of the thiazoline over those of the thiazole. The thiazoline precipitates are, in general, appreciably soluble in solutions containing alcohol, which limits the potential use of the reagent as a precipitating agent. The solubility of the chelates in organic solvents, however, should be useful in solvent extraction.

It is noteworthy that the fluorescence of 2-(*o*-hydroxyphenyl)-benzoxazole is quenched by its reaction with a transition metal ion. This may be of use in metal analysis.

ACKNOWLEDGEMENT

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SUMMARY

The reactions of the chelating reagents named in the title, with a number of metal ions, have been studied in order to evaluate the behavior of reagents containing reactive groupings analogous to those of 8-hydroxyquinoline, but so arranged as to form six-membered ring chelates with metal ions. All three reagents have been found to give less stable chelates than 8-hydroxyquinoline, indicating that for this type of reagent, six-membered ring chelates are less stable than five. 2-(*o*-Hydroxyphenyl)-benzoxazole and 2-(*o*-hydroxyphenyl)-benzothiazole have been found to be potentially useful as organic precipitating agents for metal ions, being more selective than 8-hydroxyquinoline, which they somewhat resemble in behavior. In contrast to the oxazole and thiazole, 2-(*o*-hydroxyphenyl)-benzothiazoline was found to react with most of the metal ions tried. Because of the solubility of its chelates in organic solvents, 2-(*o*-hydroxyphenyl)-benzothiazoline may be a useful solvent extraction agent for metal ions.

RÉSUMÉ

Les auteurs étudient les réactions de 3 composés avec un certain nombre d'ions métalliques en vue de déterminer le comportement de réactifs renfermant des groupements actifs analogues à ceux de la 8-hydroxyquinoléine, mais arrangés de façon à former avec les métaux des cycles de 6 chaînons. Ces 3 réactifs donnent des chélates moins stables que la 8-hydroxyquinoléine, ce qui fait supposer que les chélates à 6 chaînons sont moins stables que ceux à 5. Le 2-(*o*-hydroxyphényl) benzoxazole et le 2-(*o*-hydroxyphényl)-benzothiazole peuvent être utilisés comme réactifs de précipitation des ions métalliques; ils sont plus sélectifs que la 8-hydroxyquinoléine avec laquelle d'ailleurs ils présentent certaines analogies dans leur comportement. Contrairement à l'oxazole et au thiazole, la 2-(*o*-hydroxyphényl)-benzothiazoline réagit avec la plupart des métaux essayés. En raison de la solubilité de ses chélates dans les solvants organiques, la 2-(*o*-hydroxyphényl)-benzothiazoline peut être utilisée pour l'extraction d'ions métalliques.

ZUSAMMENFASSUNG

Die Reaktionen der obengenannten komplexbildenden Reagenzien mit mehreren Metallionen sind studiert worden, um das Verhalten der den 8-Oxychinolinanalogen Reagenzien, die Sechserringkomplexe bilden, zu erforschen. Da die Komplexe aller drei Reagenzien nicht so beständig, wie die des 8-Oxychinolins waren, kann man daraus schliessen, dass die Sechserringkomplexe nicht so beständig wie die Fünferringkomplexe sind. Es wurde festgestellt, dass 2-(*o*-Oxyphenyl)-benzoxazol und 2-(*o*-Oxyphenyl)-benzothiazol, als sehr gute Niederschlagreagenzien für Metallionen angewandt werden konnten, da sie selektiver als 8-Oxychinolin sind, dem sie im Charakter etwas ähneln. Im Gegensatz zu Oxazol und Thiazol, reagierte 2-(*o*-Oxyphenyl)-benzothiazolin mit den meisten der untersuchten Metallionen. Wegen der Löslichkeit der Komplexe von 2-(*o*-Oxyphenyl)-benzothiazolin in organischen Lösungsmitteln kann es als ein Extraktionsreagenz für Metallionen benutzt werden.

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ELEKTRONENMIKROSKOPISCHE UNTERSUCHUNGEN AUF DEM GEBIETE DER KRISTALLBILDUNG

von

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In vorangehenden Arbeiten wurden von uns in Gegenwart von Ammonnitrat gefälltes Silberjodid[1] sowie in Gegenwart von Ammonchlorid gefälltes Bariumsulfat[2] elektronenmikroskopisch untersucht. Bei der Vorbereitung dieser Versuche mussten Tröpfen der ammonsalzhaltigen Reaktionsflüssigkeiten auf dem Objektträger eingetrocknet werden. Um die elektronenmikroskopischen Aufnahmen kritisch vergleichen zu können, war es unvermeidlich notwendig, reine Ammonsalzlösungen von gleicher Konzentration nach gleicher Vorbereitung im Elektronenmikroskop zu untersuchen. Schon bei unseren Silberjodid-Versuchen[1] haben wir bemerkenswerte Beobachtungen gemacht: Bildung von schleierartigen Hüllen um die AgJ-Agglomerate, welche aber durch Einwirkung der Elektronenstrahlen verschwanden (wegsublimierten), wenn sie aus amorphen Ammonnitratkörnchen bestanden. Wurde reine Ammonitratlösung auf dem Objektträger eingetrocknet — was allerdings einige Tage dauerte — und geprüft, so konnten nur regelmässige KNO_3-Kristalle, ohne Bildung von sublimierbarer Hülle, beobachtet werden[1].

Bei unseren jetzigen Bariumsulfat-Versuchen war das Eintrocknen der Ammonchloridlösung in einem sog. Blaugelexsikkator schon innerhalb 2-3 Stunden vollkommen beendet, so dass die Untersuchung in Elektronenmikroskop vorgenommen werden konnte.

Die von uns untersuchte Ammonchloridlösung war 2%-ig. Je 1 Tropfen dieser Lösung wurde auf einem elektronenmikroskopischen Objektträger in einem Blaugelexsikkator 2-3 Stunden gehalten. Diese Zeit genügte, dass aus der Lösung Gebilde von regulärer Form sich bildeten, deren Grösse sich um etwa 2-3 μ bewegte, was ja der DARWIN-EWALD'schen[3] Theorie gut entspricht. Im Elektronenmikroskop sind nun die anfangsundurchsichtigen Ammonchloridkriställchen unter der Einwirkung der Elektronenstrahlen vom Rande ausgehend von der Ein-

Literatur S. 17.

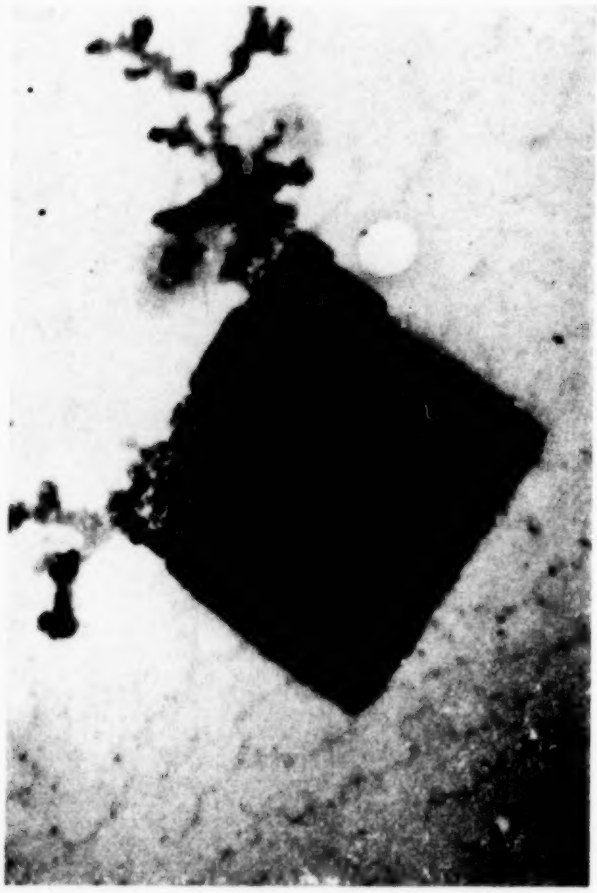

Fig. 1a. Vergr. 1:18,200

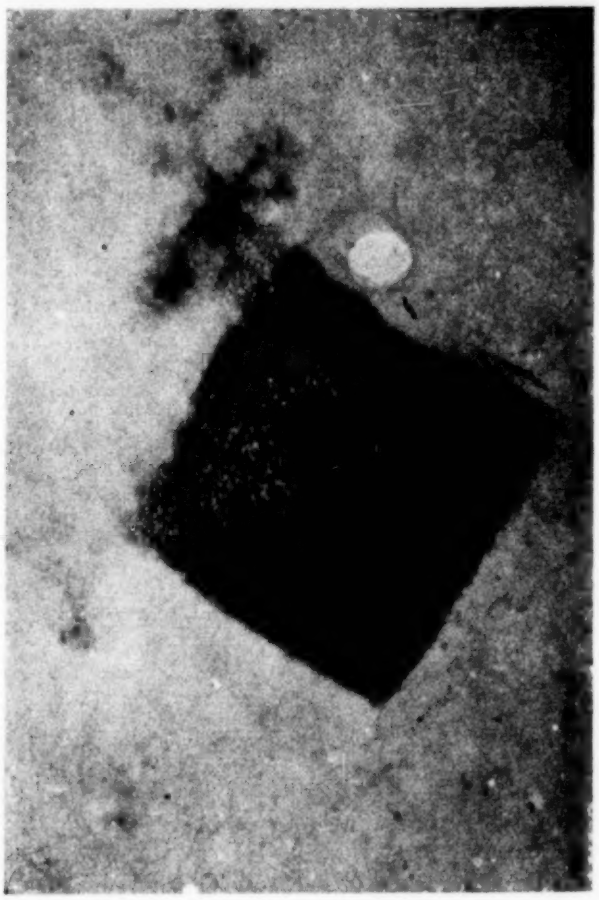

Fig. 1. Vergr. 1:16,450

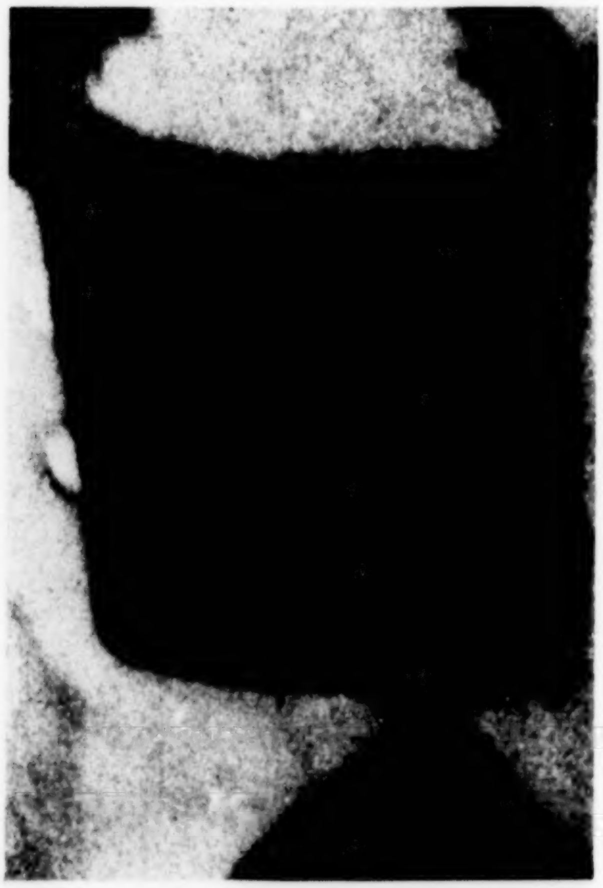

Fig. 2a. Vergr. 1:55,120

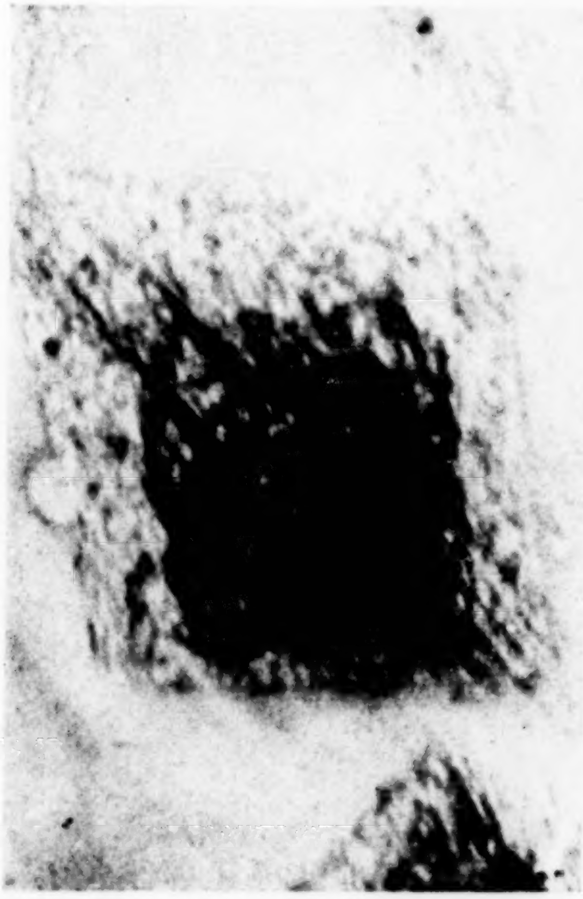

Fig. 2. Vergr. 1:49,820

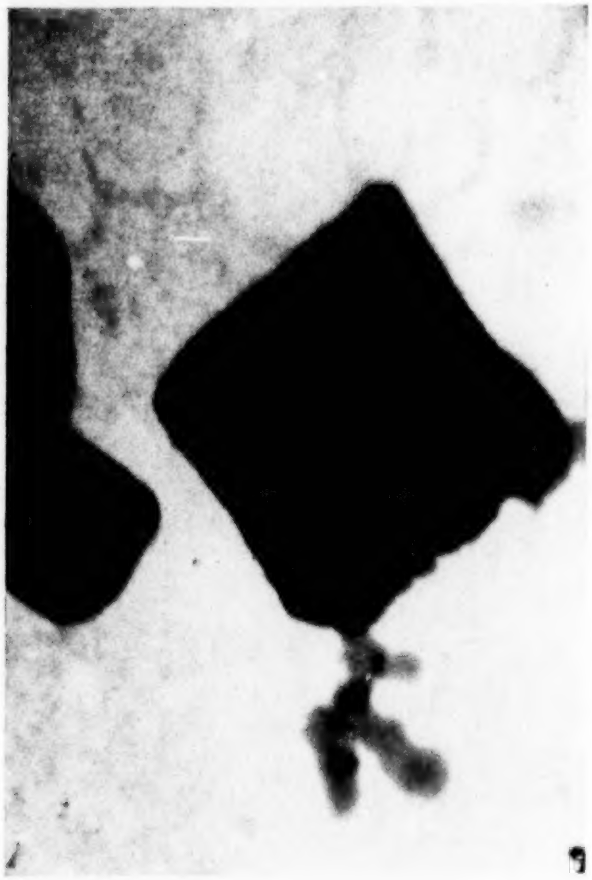

Fig. 3a. Vergr. 1:28,600

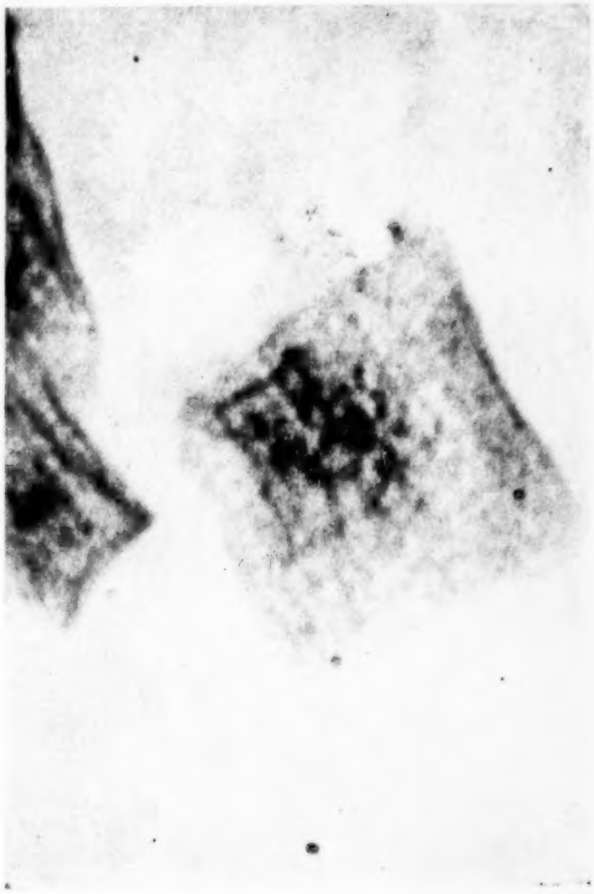

Fig. 3. Vergr. 1:25,850

Fig. 4a. Vergr. 1:8750

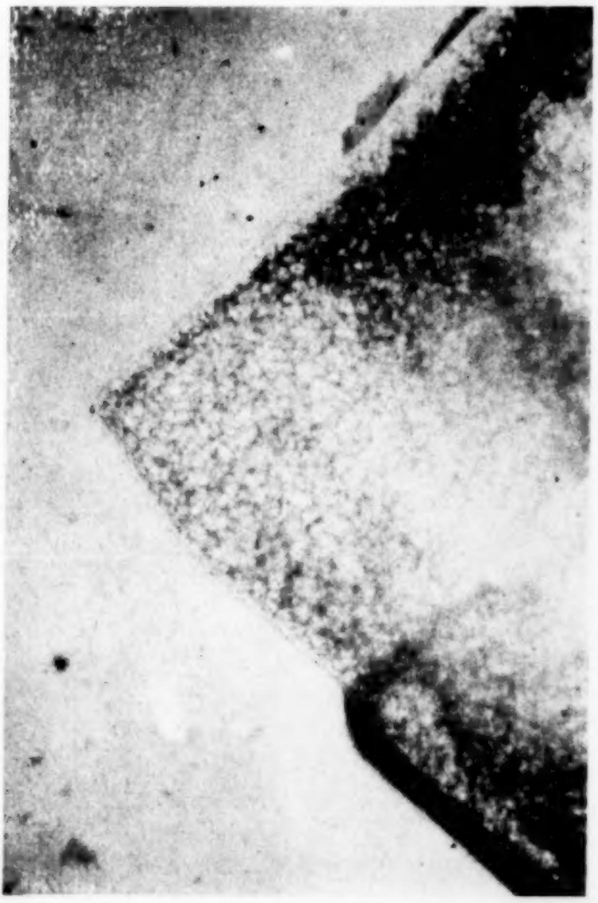

Fig. 4. Vergr. 1:8750

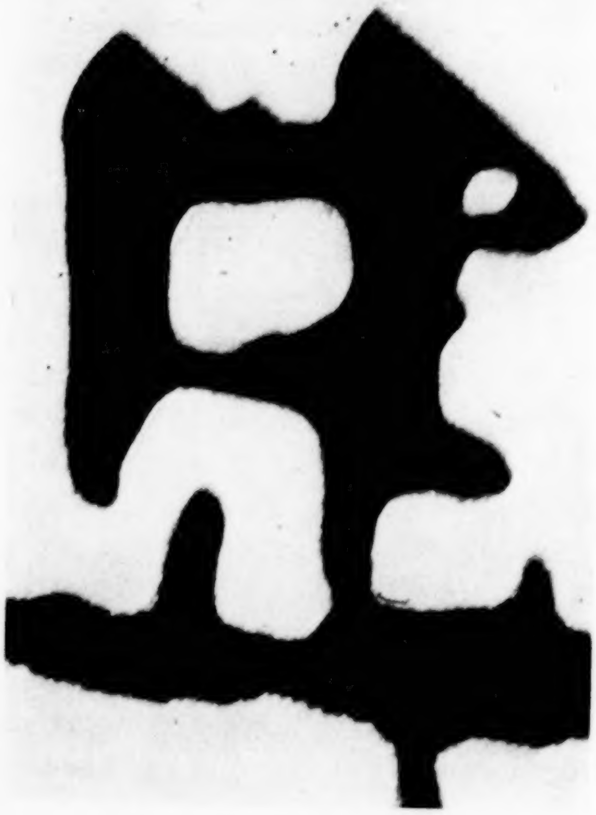

Fig. 5a. Vergr. 1:15,750

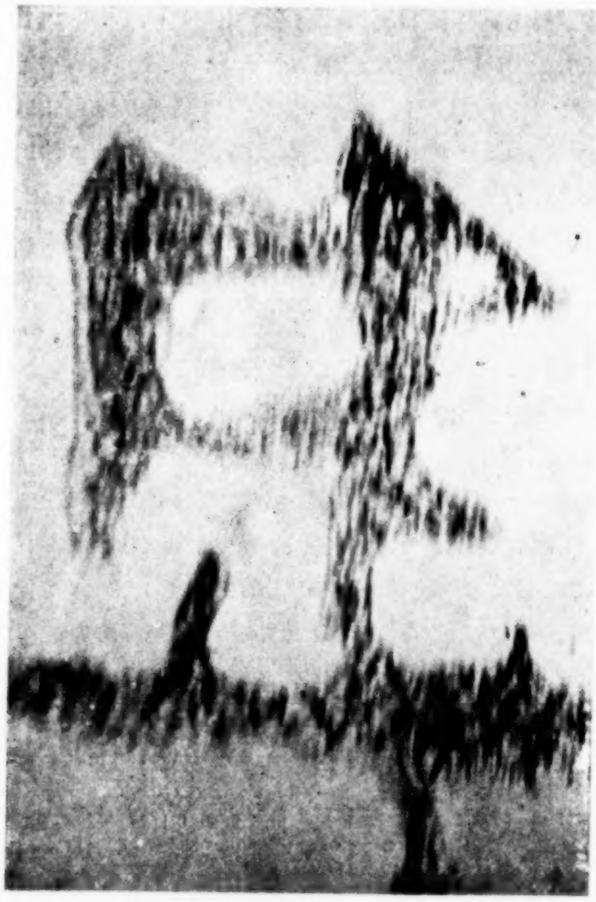

Fig. 5. Vergr. 1:15,750

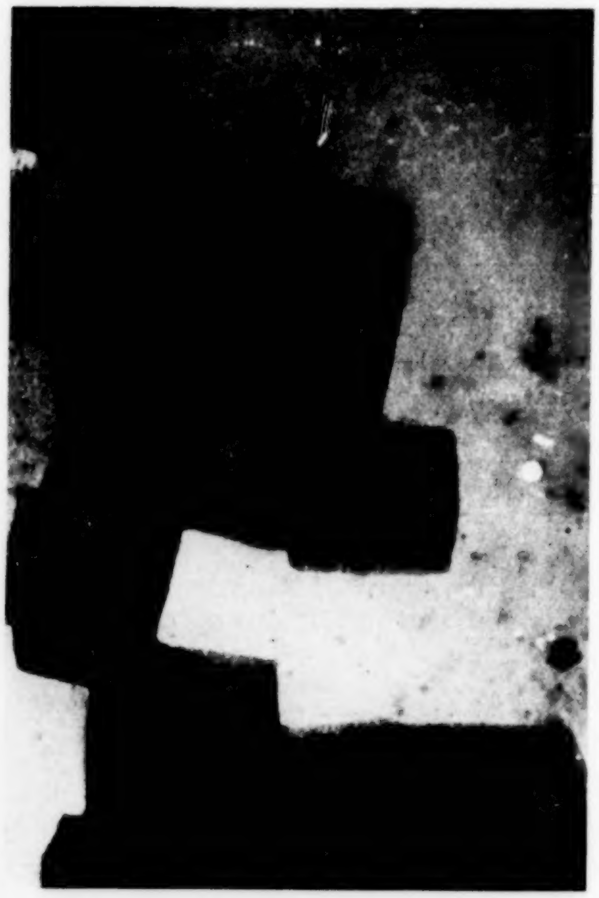

Fig. 6a. Vergr. 1:8750

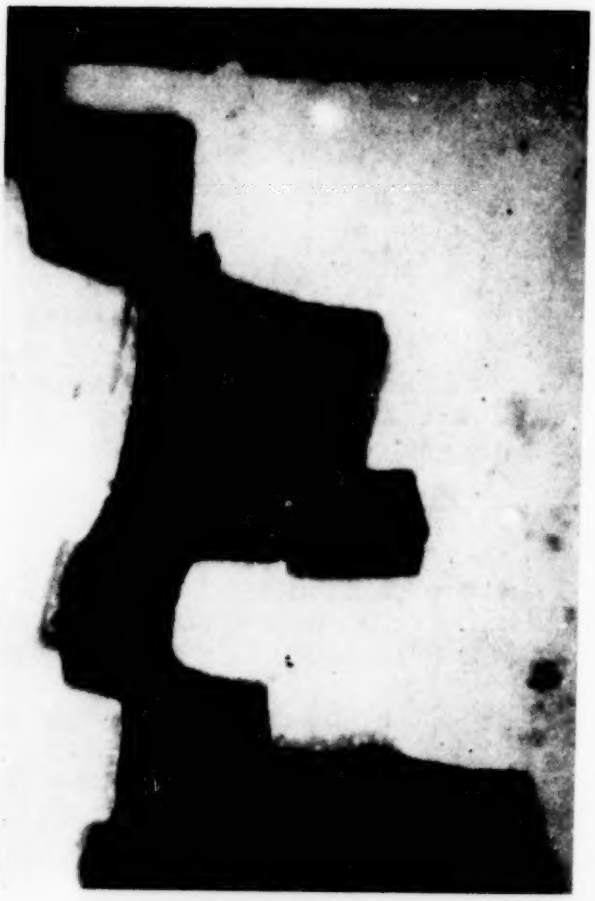

Fig. 6b. Vergr. 1:8750

strahlungsdauer abhängig durchsichtiger geworden und dabei nahmen sie eine Netzstruktur an, was auf den Aufnahmenpaaren (Aufnahmen 1a* und 1-4 a* und 4) ganz auffallend wiedergegeben ist. Wurden die elektronenmikroskopischen Präparate vor der Prüfung längere Zeit im Exsikkator gehalten, so war die durch die Elektronenbestrahlung bewirkte Aufhellung besonders in der Mitte der Aufnahme viel geringer (Aufnahme 1 bzw. 2).

Auch die dem Scheine nach amorphen Ammonchloridteilchen wurden unter dem Einfluss der Elektronenbestrahlung aufgehellt und nahmen eine Netzstruktur an (Aufnahmen 5a und 5).

Wir führten auch Versuche durch, bei welchen die Präparate nach der Bestrahlung und Aufhellung im Elektronenmikroskop d.h. in Vakuum 5-10 Minuten ohne Bestrahlung gelassen wurden um nachher wieder bestrahlt und fotographiert zu werden. Die anfangs etwas aufgehellten Kristalle mit Netzstruktur sind nun infolge Zusammenschrumpfung kleiner und von der Bestrahlungsdauer unabhängig undurchsichtbar geworden (Aufnahmen 6a und 6b; letztere ist die Aufnahme nach Schrumpfung der Netzstruktur).

Die Netzstruktur gab uns nun Gelegenheit die Knotenabstände abzuschätzen. Diese betragen etwa 5-50 mμ, was ja mit den durch SMEKAL[4] aus den Messungen von KAST[5] berechneten Daten bzw. Folgerungen in guter Übereinstimmung ist. —Nach unserer Auffassung sind die elementaren Kristalle („Gitterblöcke") des Ammonchlorids dadurch sichtbar geworden, dass das aus der Lösung intermediär in amorphem Zustand ausgeschiedene Ammonchlorid wegsublimiert worden ist.

Unsere den Mechanismus der Kristallbildung betreffenden Vorstellungen gedenken wir nach Abschluss von unseren chemischen Untersuchungen zu veröffentlichen.

Für die technische Mithilfe möchten die Autoren ihren wärmsten Dank Frl. SZIVESSY aussprechen.

ZUSAMMENFASSUNG

Verfasser haben versucht die Mikrostruktur der Ammonchloridkristalle elektronenmikroskopisch zu verfolgen. Die Ergebnisse weisen auf die Richtigkeit der KAST-SMEKALschen Vorstellung hin.

SUMMARY

The authors have tried to establish the microstructure of ammonium chloride by means of the electron microscope. The results confirm the accuracy of the KAST-SMEKAL representation.

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* Die mit arabischen Zahlen und mit „a" bezeichneten Aufnahmen sind nach ganz kurzer Zeit nach dem Einlegen des Präparates in das Elektronenmikroskop, die nur mit arabischen Zahlen bezeichneten erst nach einer, eine bestimmte Zeit dauernde Elektronenbestrahlung aufgenommen.

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RÉSUMÉ

Les auteurs ont essayé d'établir la microstructure des cristaux de chlorure d'ammonium au microscope électronique. Les résultats confirment l'exactitude de la représentation de KAST-SMEKAL.

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NEW OBSERVATIONS ON THE SOLUBILITY OF PRUSSIAN BLUE

by

MORITZ KOHN *

It was reported some time ago[1] that sodium pyrophosphate reacts with Prussian blue, whereby decoloration takes place because a clear solution of sodium ferrocyanide and ferric sodium pyrophosphate results. However, it had been observed that also sodium metaphosphate** dissolves Prussian blue forming sodium ferrocyanide and ferric sodium metaphosphate:

$$12NaPO_3 + xNaPO_3 + Fe_4[Fe(CN)_6]_3 = 3Na_4[Fe(CN)_6] + [4Fe[PO_3]_3.xNaPO_3]$$

Small quantities of sodium metaphosphate peptize the Prussian blue. This fact can be explained as was done already in former cases[2] by the formation of water-soluble colloidal Prussian blue (sodium ferric ferrocyanide):

$$3NaPO_3 + Fe_4[Fe(CN)_6]_3 = 3NaFe[Fe(CN)_6] + Fe(PO_3)_3$$

Potassium metaphosphate could not be used because it is insoluble in water. However, an equimolecular mixture of potassium metaphosphate and sodium metaphosphate can be melted easily. This glassy potassium sodium metaphosphate is soluble in water and this solution reacts with Prussian blue in the same way as sodium metaphosphate. Small quantities of sodium pyrophosphate, or sodium pyrophosphate in presence of very small quantities of alkali carbonate, also peptize Prussian blue:

$$Na_4P_2O_7 + Fe_4[Fe(CN)_6]_3 = 3NaFe[Fe(CN)_6] + NaFeP_2O_7.$$

If metaphosphates are melted after addition of alkali carbonates polyphosphates are formed, for instance, a substance of the composition of sodium triphosphate:

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** By sodium metaphosphate always sodium hexametaphosphate $(NaPO_3)_6$ is meant in this paper.

$$3NaPO_3+Na_2CO_3=Na_5P_3O_{10}+CO_2.$$

and sodium tetraphosphate:

$$4NaPO_3+Na_2CO_3=Na_6P_4O_{13}+CO_2.$$

These glassy polyphosphates are easily soluble in water. Frankenthal, Roberts and Neuberg[3] have found already that solutions of sodium triphosphate react with Prussian blue, whereby decoloration takes place forming alkali ferrocyanide and alkali ferric polyphosphates. Smaller quantities of these polyphosphates yield colloidal solutions of alkali ferric ferrocyanide. The cleaning material "calgon" is sodium hexametaphosphate and the alkaline detergent and cleaning material "calgonite"[4] also contains as principal ingredient sodium hexametaphosphate. After neutralization by an acid, solutions of calgonite dissolve Prussian blue and smaller quantities of calgonite peptize Prussian blue. Inorganic substances which can peptize Prussian blue have not been known up to the present time. However, it had been known for many years that potassium ferrocyanide peptizes Prussian blue. But potassium ferrocyanide can be considered both an inorganic and an organic substance.

Furthermore, some observations on the solubility of Prussian blue in organic compounds are reported. The neutral alkali salicylates (the monosodium and monopotassium salt) dissolve Prussian blue forming solutions containing alkali ferrocyanides and ferric alkali salicylates. If to the sodium salicylate such a small quantity of sodium carbonate is added that the mixture is slightly alkaline, the solution of Prussian blue is facilitated and a clear yellowish brown solution of sodium ferric salicylate and sodium ferrocyanide results.

$$Fe_4[Fe(CN)_6]_3+12C_7H_5O_3Na+xC_7H_5O_3Na=3Na_4[Fe(CN)_6]+[4(C_7H_5O_3)_3Fe \\ .xC_7H_5O_3Na]$$

In the same way the potassium salt of β-resorcylic acid (2, 4-dihydroxybenzoic acid) reacts with Prussian blue, whereby yellowish brown solutions of the ferric potassium salt of β-resorcylic acid and potassium ferrocyanide are formed):

$$Fe_4[Fe(CN)_6]_3+12C_7H_5O_4K+xC_7H_5O_4K=3K_4[Fe(CN)_6]+[4(C_7H_5O_4)_3Fe \\ .xC_7H_5O_4K]$$

By the reaction of smaller quantities of alkali salicylates or of alkali salicylates in the presence of alkali carbonates or of the alkali salts of β-resorcylic acid colloidal Prussian blue is obtained:

$$3C_7H_5O_3Na+Fe_4[Fe(CN)_6]_3=3NaFe[Fe(CN]_6]+(C_7H_5O_3)_3Fe$$
$$C_7H_5O_4Na+Fe_4[Fe(CN)_6]_3=3NaFe[Fe(CN)_6]+(C_7H_5O_4)_3Fe$$

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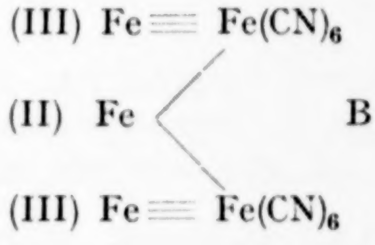
But we have to bear in mind that neither salicylic acid nor β-resorcylic acid can peptize the Prussian blue. Although neutral alkali tartrates, trisodium citrate, disodium citrate and monosodium citrate, as was found earlier, can peptize the Prussian blue to the colloidal Prussian blue, neither tartaric acid nor citric acid can produce colloidal Prussian blue. Therefore, it is self-evident that potassium or sodium ions must be present because otherwise neither $KFe[Fe(CN)_6]$ nor $NaFe[Fe(CN)_6]$ can be formed. PAPPADÁ[7] reported that organic acids and organic acids containing one or more hydroxy groups can peptize Prussian blue. The facts mentioned above prove that PAPPADÁ's statement is erroneous. Only one case has been found so far, the case of the oxalic acid which is the only free acid that can peptize Prussian blue. But a different explanation is necessary for the peptizing action of oxalic acid* than for the peptizing action of the substances listed in this paper.

On the other hand, PAPPADÁ's[8] observation that certain organic substances, for instance, glucose or glycerol, do not precipitate colloidal solutions of Prussian blue could be confirmed.

In the colloidal solutions of Prussian blue in alkali metaphosphates, alkali polyphosphates, alkali salicylates, alkali β-resorcylates a blue precipitate gradually settles. But it has to be considered that only the alkali ferric ferrocyanide forms the colloidal solutions, while the other substances formed in the reactions, for instance, ferric metaphosphate, are insoluble in water and can settle and this precipitate can also adsorb the blue dye. In spite of this fact, a part of the colloidal blue is retained in these solutions and these solutions are relatively stable. In his classical researches on the colloidal Prussian blue GRAHAM[9] reported that Turnbull's blue can not be peptized by potassium oxalate as the Prussian blue. This statement is erroneous. Turnbull's blue prepared by precipitation of 3 moles ferrous sulfate with 2 moles potassium ferricyanide should be either the ferrous ferricyanide (A) or the ferrous ferric ferrocyanide (B),

$$\text{(II) } Fe_3[Fe(CN)_6]_2$$

A



B

as it was explained in a former paper[10]. Moreover, it was mentioned there that Turnbull's blue differs from Prussian blue in not being completely dissolved in potassium oxalate. This reaction was interpreted by the decomposition of 2 moles of Turnbull's blue into one mole Prussian blue

$$2Fe_3[Fe(CN)_6]_2 = Fe_4[Fe(CN)_6]_3 + Fe_2[Fe(CN)_6]$$

and one mole of the white ferrous ferrocyanide. The latter is insoluble in potassium

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* See T. R. BOLAN AND W. TAYLOR, *Trans. Faraday Soc.*, 35 (1939) 268.

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oxalate. However, if only small additional quantities of potassium oxalate are present peptization of the dye takes place. The part which is peptized is the Prussian blue, while the white ferrous ferrocyanide remains undissolved. It can be observed that in the mixture of Turnbull's blue and potassium oxalate a whitish sediment, obviously the ferrous ferrocyanide, settles, which is covered by the blue colloidal solution of Prussian blue. This solution is stable if protected from light*. If we assume that Turnbull's blue has the afore-mentioned structure (A or B) we have moreover to make the improbable assumption that even the very diluted solutions of potassium oxalate can split the great molecule of Turnbull's blue (A or B) at ordinary temperature. Therefore it seems far more probable that Turnbull's blue is already a mixture of the products of the decomposition of the great molecule (A or B), *i.e.*, of equal molecules of Prussian blue and ferrous ferrocyanide.

DE KONINCK[11] observed that Prussian blue does not react with hydrobromic acid. This is also an erroneous statement. Only rather diluted hydrobromic acid does not attack Prussian blue. But hydrobromic acid of 48% dissolves Prussian blue to a clear yellowish brown solution. If this mixture is kept at room temperature for some hours and diluted afterwards, a small part of the Prussian blue is still precipitated. But if the mixture is diluted after a longer time, no Prussian blue is precipitated because the dye has already been destroyed.

Reactions of Prussian blue with alkali metaphosphates

I. 5 g sodium metaphosphate were dissolved in 20 ml water, 0.55 ml 0.1*M* ferric nitrate and 0.43 ml 0.1*M* potassium ferrocyanide were mixed and to this precipitate of Prussian blue 6 ml of the metaphosphate solution were added. By heating, a slightly greenish blue solution was obtained. This solution was kept overnight and filtered afterwards. The filter was washed with the sodium metaphosphate solution. The clear filtrate was precipitated with potassium hydroxide, whereby it yielded 0.0041 g Fe_2O_3. The calculated weight of Fe_2O_3 is 0.0043 g.

II. 0.55 ml 0.1*M* ferric nitrate and 0.43 ml 0.1*M* potassium ferrocyanide were mixed. To this precipitate of Prussian blue 10 ml water were added and 1 ml of the sodium metaphosphate solution used in I. By shaking, a colloidal solution was prepared.

III. An equimolecular mixture of KH_2PO_4 and $NaH_2PO_4 + 2\ H_2O$ was melted. When the crucible had cooled, it contained the clear glassy sodium potassium hexametaphosphate which is easily soluble in water. 8.5 g of this metaphosphate were dissolved in water to a volume of 35 ml. 1.14 ml 0.1*M* ferric nitrate and 0.86 ml 0.1*M* potassium ferrocyanide were mixed and to the precipitate of Prussian blue 10 ml of the potassium sodium metaphosphate solution were added. The mixture was heated until no change could be observed, filtered and the filter washed with the metaphosphate solution. The filtrate precipitated with potassium hydroxide gave 0.0073 g Fe_2O_3 instead of the calculated weight of 0.0091 g Fe_2O_3.

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* It is shown in the experimental part, that even a 0.83% solution of potassium oxalate dissolves Turnbull's blue. In the light green solution containing $K_4[Fe(CN)_6]$ and $K_3[Fe(C_2O_4)_3]$ the calculated quantity of a white precipitate of $Fe_2[Fe(CN)_6]$ settles.

IV. To 2 ml of the suspension of Prussian blue (precipitated by mixing 1.14 ml 0.1*M* ferric nitrate with 0.86 ml 0.1*M* potassium ferrocyanide), 5.5 g of the potassium sodium metaphosphate solution used in III were added and of a solution of 0.2 g sodium carbonate in 10 ml water until on heating a clear solution was obtained. For this purpose about 4 ml of Na_2CO_3 were used up.

If hydrochloric acid is added to the cold mixture, the solution remains clear for some hours. Later the blue color begins to appear. On the next day Prussian blue was already precipitated and the dye covered the wall of the test tube.

V. On mixing 2 ml of the suspension of Prussian blue, 26 ml water and 2 ml of the sodium potassium metaphosphate solution used in III colloidal Prussian blue was obtained.

Preparation of colloidal Prussian blue by the reaction with sodium pyrophosphate

I. 0.4 sodium pyrophosphate dissolved in 10 ml water and a precipitate of Prussian blue (prepared by mixing 4 ml 0.1*M* ferric nitrate and 3 ml 0.1*M* potassium ferrocyanide) and 5 ml glycerol dissolved in 15 ml water were mixed. A colloidal solution of Prussian blue resulted.

II. 5 ml 0.1*M* ferric nitrate, 3 ml 0.1*M* potassium ferrocyanide, 7 ml water, 0.7 g $Na_4P_2O_7 + 10\ H_2O$ and 5 ml glycerol dissolved in 15 ml water were mixed in order to prepare colloidal Prussian blue.

III. 0.3 g $Na_4P_2O_7 + 10\ H_2O$ and 2 ml of the sodium carbonate solution used in IV (in experiment IV with potassium sodium metaphosphate) were diluted to a volume of 27 ml. 6 ml of this alkaline pyrophosphate solution and a suspension of 3 ml Prussian blue (prepared by mixing of 1.29 ml 0.1*M* potassium ferrocyanide and 1.71 0.1*M* ferric nitrate) and 9 ml water gave a colloidal solution.

Reaction of Prussian blue with sodium tetraphosphate

I. 5 ml of a suspension of Prussian blue (prepared by mixing of 2.85 ml 0.1*M* ferric nitrate and 2.15 ml 0.1*M* potassium ferrocyanide), 10 ml water and 2 ml of the sodium tetraphosphate solution used in III yielded colloidal Prussian blue.

II. 2 ml of the suspension of Prussian blue and 20 ml of the sodium tetraphosphate solution used in III gave, when heated gently, a clear solution.

III. 5 ml of the Prussian blue suspension, 10 ml water, 1.5 ml of a solution of sodium tetraphosphate (4 g sodium tetraphosphate mixed with 40 ml water) and 1 ml of a sodium carbonate solution (0.5 g sodium carbonate dissolved by addition of water to a volume of 50 ml) yielded a colloidal solution.

Reactions of polyphosphates with Prussian blue

I. 7 g $NaH_2PO_4 + 2\ H_2O$ and 0.7 g Na_2CO_3 were melted together until the generation of CO_2 stopped. 3.4 g of this glassy melt were dissolved in 10 ml water. 4 ml of this polyphosphate solution were mixed with 1 ml of the suspension of Prussian blue whereby a clear colorless solution resulted.

II. 7 ml of the suspension of Prussian blue (prepared by precipitation of 4 ml 0.1*M* ferric nitrate with 3 ml 0.1*M* potassium ferrocyanide), 8 ml water and 0.5 ml of the polyphosphate solution used in I gave colloidal Prussian blue.

Reactions of alkali salicylates with Prussian blue

I. 1.33 ml 0.1*M* ferric nitrate and 1 ml 0.1*M* potassium ferrocyanide were mixed. Water was added and 9 g of (neutral) monosodium salicylate. The mixture was heated and water was added to a volume of 250 ml. A dark brown liquid resulted, but the solution was clear. A sample diluted in the test tube with more water was light brown and remained clear.

II. 1.33 ml 0.1*M* ferric nitrate, 1 ml 0.1*M* potassium ferrocyanide were mixed, 10 ml water were added and 2 ml of the 250 ml solution (prepared in experiment I). On shaking, peptization of the Prussian blue took place.

III. To 1.33 ml 0.1*M* ferric nitrate 1 ml 0.1*M* potassium ferrocyanide was added and 10 g monopotassium salicylate afterwards. On dilution to a volume of 80 ml with water and heating, a dark brown mixture was obtained. When moreover 170 ml water were added no turbidity could be observed.

IV. 1.33 ml 0.1*M* ferric nitrate, 1 ml potassium ferrocyanide, 15 ml water and 3 ml of the 250 ml solution (prepared in III) were mixed and shaken afterwards, whereby a colloidal solution was obtained.

V. 1 g monosodium salicylate which was made slightly alkaline by addition of sodium carbonate was dissolved to a volume of 10 ml in water and a precipitate of 0.57 ml 0.1*M* ferric nitrate with 0.43 ml 0.1*M* potassium ferrocyanide was added. The color becomes dark brown in the cold and on heating, a clear yellowish brown solution is formed. Should in such experiments a brown precipitate appear after heating, too much sodium carbonate was used. (1 g sodium salicylate and 0.1 g potassium carbonate give also a clear yellowish brown solution.)

VI. To 3.2 g salicylic acid (1 mol) 1.3 g sodium carbonate (0.5 mol) was added and water to a volume of 40 ml. The mixture was heated on the water bath until the generation of CO_2 stopped. To Prussian blue prepared by mixing 2 ml 0.1*M* ferric nitrate and 1 ml 0.1*M* potassium ferrocyanide, 30 ml of the sodium salicylate solution were added. By heating on the water bath a clear brown solution resulted. On addition of hydrochloric acid to this solution salicylic acid is precipitated and the color of Prussian blue appears simultaneously. If the mixture is diluted so far that hydrochloric acid does not produce a precipitate of salicylic acid the blue color also appears.

VII. To 3.2 g salicylic acid (1 mol) and 1.7 g sodium carbonate (2/3 mol) water was added to a volume of 30 ml. The mixture was heated on the water bath in order to remove the CO_2. The solution was cooled and Prussian blue, precipitated by mixing 2 ml 0.1*M* ferric nitrate and 1.5 ml 0.1*M* potassium ferrocyanide, was added. A clear brown solution was formed at room temperature after one hour.

Reactions of alkali β-resorcylates with Prussian blue

I. To 6 g β-resorcylic acid (1 mol) and 3 g potassium carbonate ($\frac{1}{2}$ mol K_2CO_3 = 2.69 g) water was added to a volume of 30 ml. The mixture was heated on the water bath until the generation of CO_2 stopped. To this cooled solution was added a precipitate of Prussian blue prepared by mixing 1.33 ml 0.1*M* ferric nitrate and 1 ml 0.1*M* potassium ferrocyanide. By heating on the water bath, a clear yellowish brown solution was obtained in a short time.

II. 10 ml of the solution of Prussian blue prepared in I were diluted to 50 ml. 2 ml of this diluted solution were used to peptize a suspension of Prussian blue formed by mixing 1.33 ml 0.1*M* ferric nitrate and 1 ml potassium ferrocyanide.

III. To 7.5 g β-resorcylic acid (1 mol) and 3.5 potassium carbonate ($\frac{1}{2}$ mol K_2CO_3 = 3.36 g) water was added to a volume of 55 ml. By heating on the water bath potassium β-resorcylate was prepared. 25 ml of the solution of potassium β-resorcylate and a precipitate of Prussian blue formed by mixing 0.57 ml 0.1*M* ferric nitrate and 0.43 ml 0.1*M* potassium ferrocyanide were heated on the water bath. A clear yellowish brown solution was obtained.

IV. 0.55 ml 0.1*M* ferric nitrate and 0.43 ml 0.1*M* potassium ferrocyanide were mixed. To the precipitate of Prussian blue 15 ml water were added and 1 ml of the potassium β-resorcylate solution prepared in III. The mixture was shaken, whereby a colloidal solution of Prussian blue was obtained.

V. To 7.2 g β-resorcylic acid (1 mol) and 2.6 g sodium carbonate ($\frac{1}{2}$ mol Na_2CO_3 = 2.4 g) water was added to a volume of 43 ml. A solution of sodium β-resorcylate was prepared by heating on the water bath. 1 ml of this cooled solution, 15 ml water and 1 ml of a suspension of Prussian blue (prepared by precipitating 0.55 ml 0.1*M* ferric nitrate with 0.44 ml potassium ferrocyanide) were mixed. By shaking, a colloidal solution was obtained.

Peptization of Turnbull's blue by potassium oxalate

I. To 0.2021 g $FeSO_4 + 7\ H_2O$ (3 moles) dissolved in water were added 4.84 ml 0.1*M* potassium ferricyanide (2 moles) and water to a volume of 18 ml of the mixture.

a. 9 ml of this well shaken suspension of Turnbull's blue were mixed with 0.1 g potassium oxalate dissolved in 5 ml water. 10 ml water were added one hour later. A colloidal solution could be prepared by shaking. This colloidal solution was not precipitated when 2 g glucose dissolved in 20 ml water were added.

b. This reaction was carried out in the same way as the reaction a) with 9 ml of the suspension of Turnbull's blue. But 0.2 g potassium oxalate were added. In this case no colloidal solution could be obtained, but after some days a greenish liquid resulted which contained a light precipitate of ferrous ferrocyanide, the insoluble residue of the decomposition of the dye. The mixture was filtered, the precipitate washed with diluted hydrogen peroxide and sodium chloride whereby complete oxidation took place. By the decomposition with ammonia 0.0127 g Fe_2O_3 were obtained instead of the calculated weight of 0.0097 g Fe_2O_3.

II. 0.2854 g $FeSO_4 + 7\ H_2O$ (3 moles) were dissolved in 18 ml water and 6.84 ml 0.1*M* potassium ferricyanide (2 moles) were added; the mixture was shaken. A solution of 0.1 g potassium oxalate in 5 ml water was added after four days and the mixture was shaken again. A colloidal solution was formed. The addition of a solution of 4.5 ml glycerol in 15.5 ml water did not produce a precipitation.

Both in I and in II the colloidal solutions deposit a whitish sediment, obviously the ferrous ferrocyanide.

Reaction of Prussian blue with hydrobromic acid

2 ml 0.1*M* ferric nitrate and 1.5 ml 0.1*M* potassium ferrocyanide were mixed and hydrobromic acid (48%) was added to a volume of 100 ml. A clear brown solution was obtained.

I. 50 ml were diluted with water to a volume of 500 ml. 20 g sodium bromide were added to this green solution in order to precipitate the Prussian blue. The Prussian blue was filtered, washed with sodium bromide solution and afterwards with water. The decomposition with potassium hydroxide produced 0.0032 g Fe_2O_3. If the Prussian blue had not reacted with the hydrobromic acid 0.0160 g Fe_2O_3 would be formed. Therefore, 80% of the Prussian blue was destroyed.

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II. 25 ml were heated on the water bath to 70° for some minutes. The color did not change, and if this mixture was diluted with water no Prussian blue was precipitated.

III. 25 ml were kept at room temperature two days. If water was added no precipitation of Prussian blue occurred.

SUMMARY

1. Alkali metaphosphates and alkali polyphosphates dissolve Prussian blue to potassium ferrocyanide and to the corresponding ferric alkali metaphosphates and polyphosphates. But smaller quantities peptize Prussian blue. The alkali metaphosphates and alkali polyphosphates are the first inorganic substances whose peptizing action on Prussian blue was observed.

2. The alkali salicylates and alkali β-resorcylates react in an analogous way with Prussian blue. They dissolve Prussian blue if sufficient quantities are present. But smaller quantities yield colloidal Prussian blue.

3. The statement in the literature that Turnbull's blue is not peptized by potassium oxalate is erroneous. Simultaneously, the conclusion had to be drawn that Turnbull's blue is an equimolecular mixture of Prussian blue and ferrous ferrocyanide.

4. Data given in the literature describing some reactions leading to colloidal Prussian blue and stating that Prussian blue does not react with hydrobromic acid are erroneous.

RÉSUMÉ

1. Les métaphosphates et polyphosphates alcalins dissolvent le bleu de Prusse en ferrocyanure de potassium et en méta- et polyphosphates alcalins et ferriques. Mais de plus faibles quantités peptisent le bleu de Prusse. Les méta- et polyphosphates alcalins sont les premiers composés connus ayant une action peptisante sur le bleu de Prusse.

2. Les salicylates et β-résorcylates alcalins réagissent de la même façon avec le bleu de Prusse. En quantité suffisante, ils dissolvent le bleu de Prusse. Mais de plus faibles quantités conduisent à la formation de bleu de Prusse colloïdal.

3. Contrairement à ce que l'on dit dans la littérature, le bleu de Turnbull n'est pas peptisé par l'oxalate de potassium. D'autre part, on doit considérer le bleu de Turnbull comme un mélange équimoléculaire de bleu de Prusse et de ferrocyanure ferreux.

4. Certaines indications bibliographiques sur des réactions conduisant au bleu de Prusse colloïdal sont fausses. Le fait que le bleu de Prusse ne réagit pas avec l'acide bromhydrique est faux également.

ZUSAMMENFASSUNG

1. Alkalimetaphosphate sowie Alkalipolyphosphate lösen Berlinerblau zu Alkaliferrozyanid und den entsprechenden Alkaliferrimetaphosphaten und Alkaliferripolyphosphaten. Kleinere Quantitäten der genannten Phosphate bilden kolloides Blau. Die Alkalimetaphosphate und Alkalipolyphosphate sind die ersten rein anorganischen Substanzen, deren peptisierende Wirkung auf das Berlinerblau beobachtet wurde.

2. Alkalisalizylate und Alkali β-Resorzylate reagieren in analoger Weise mit Berlinerblau. Sie lösen es vollständig, wenn sie in ausreichenden Quantitäten vorhanden sind. Kleinere Quantitäten bilden kolloides Blau.

3. Die Angabe in der Literatur, dass Turnbulls Blau durch Kaliumoxalat nicht peptisiert wird, ist unrichtig. Gleichzeitig musste der Schluss gezogen werden, dass das Turnbulls Blau ein äquimolekulares Gemenge von Berlinerblau und Ferroferrozyanid ist.

4. Eine Literaturangabe bezüglich einiger Reaktionen, die zum kolloiden Blau führen und eine weitere Angabe, dass Berlinerblau nicht mit Bromwasserstoffsäure reagiert, sind unrichtig.

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A METHOD FOR THE TITRIMETRIC DETERMINATION OF SULFATE USING THE DISODIUM SALT OF ETHYLENEDIAMINETETRA-ACETIC ACID

by

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The gravimetric method for the determination of sulfate as barium sulfate is very laborious and time-consuming. Though there are various titrimetric procedures *e.g.* with barium chromate or benzidine, they have the disadvantage that the precipitate which is formed must be filtered quantitatively. Also these methods are not always very accurate. The titrimetric analysis with tetrahydroxyquinone as an internal indicator seems to be much better, but the end-point of the titration of sulfate by a barium chloride solution is slow and very indistinct and the results inaccurate[1,2].

MUNGER, NIPPLER AND INGOLS[3] precipitated sulfate in a slightly acid solution with a known excess of barium chloride, boiled for a few seconds, cooled and then titrated the excess of barium ions with a solution of the disodium salt of ethylenediaminetetra-acetic acid. This end-point was not very distinct and they therefore added a known amount of magnesium chloride which they found gave a sharp end-point.

In a previous paper[4] the author has described a method for the titration of barium ions, which works well. Although the titration of barium chloride solutions was accurate, however, calculation of the sulfate content from the difference of the added and the titrated excess of barium chloride gave low results for sulfate.

MUNGER, NIPPLER AND INGOLS made a separate test to titrate the alkalinity; then they added the same amount of acid to their sample to destroy all the carbonates. In my experiments I always added 1 ml $2N$ hydrochloric acid to make the solution sufficiently acid.

In my previous paper[4] I mentioned that it was necessary to increase the amount of ammonia in the buffer solution and to use 4 ml of it to increase the pH (which has become too low after the addition of 1 ml $2N$ HCl) from 9.90 to 10.1.

In agreement with MUNGER, it was found unnecessary to remove the barium sulfate precipitate before the titration of the excess of barium chloride.

In the titration of a solution containing 100.0 mg SO_4^{-2} per litre I obtained low results, when the titration was done directly after boiling for some seconds and cooling (*e.g.* 84.4 mg SO_4^{-2}/litre).

Boiling for times up to two hours and titrating after cooling, gave somewhat better results. When the solution was kept warm overnight I found 99.1 mg SO_4^{-2}/l.

In Table I some data are given from samples, boiled for five minutes and the excess of barium chloride titrated after different times. Although the results for sulfate calculated from the data from these experiments were not always reproducible, we can ascertain that the time has a pronounced influence on the formation of the barium sulfate precipitate and when the excess of barium ions is titrated on the following day, we get more exact figures.

TABLE I

THE INFLUENCE OF THE TIME ON THE FORMATION OF THE BARIUM SULFATE PRECIPITATE AFTER BOILING FOR FIVE MINUTES. USED 100 ml OF A SOLUTION, CONTAINING 100.0 mg SO_4^{-2} PER LITRE

Time in hours elapsed after boiling	mg SO_4^{-2}/l titrated
1	89.4
2	92.8
4	97.0
6	97.8
24	99.2 99.3 (duplo)

We see that, under these circumstances, after six hours the titrated amount of sulfate was still too low, but after 24 hours we found nearly the exact amount.

To check this method different amounts of sulfate were then titrated after 24 hours. The data found are given in Table II; the amounts of sulfate found were nearly the same as the amounts added.

TABLE II

TITRATION OF DIFFERENT AMOUNTS OF SULFATE WITH THE DISODIUM SALT OF ETHYLENEDIAMINETETRA-ACETIC ACID AFTER 24 HOURS

mg SO_4^{-2}/l added	mg SO_4^{-2}/l found
10.0	11.0
25.0	25.7
50.0	50.1
100.0	99.0
200.0	198.0

In determining the sulfate content of tap water, besides the excess of barium ions, the calcium and magnesium ions of the total hardness are also titrated. By subtracting the total hardness, which must be titrated separately, we find the excess of barium chloride. From the difference of the added amount and the excess of barium chloride, the sulfate content is calculated.

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TABLE III

SULFATE CONTENT OF SAMPLES OF TAP WATER AND ALSO OF SOFTENED TAP WATER DETERMINED BOTH GRAVIMETRICALLY AND TITRIMETRICALLY IN mg SO_4^{-2}/l

Sample number	not softened				softened			
	grav.		titr.		grav.		titr.	
1.	76.0	75.9	76.1	76.2			76.4	76.3
2.	73.2	73.8	73.2	72.7			73.3	73.2
3.	59.4	59.2	59.6	59.4	59.0	58.8	59.3	59.3

In Table III are given some results for the sulfate content of samples of tap water determined both titrimetrically and gravimetrically (column 1 and 2), and it will be seen that there is good agreement.

However, when the sulfate content is low or the total hardness high, the error in correcting for the hardness will become much higher.

Therefore it is advisable to remove the calcium and magnesium ions by filtering through a cation exchanger.

As an ion exchanger we used a glass tube, 1.6 cm diameter and 35 cm long, closed at the lower end with a glass tap. On a support of some glasswool we put a layer of 25 cm of Dowex 50 cation exchanger (± 50 ml of cation exchanger). At the upper end we put a glass funnel. In this filter the water had been softened to zero hardness. A side tube, fitted just above the layer of the ion exchanger, is very useful for removing the excess of the sample or washing liquid.

In our experiments we found that 50 ml of water was sufficient to remove the water from the preceding sample.

The filter is regenerated with a solution of 30 g of NaCl in 100 ml of distilled water, passed very slowly through the filter. The salt solution is then washed out with distilled water. When we carefully rinsed away all the salt solution from the funnel with portions of 10 ml of water, we found that 60 to 70 ml of water was sufficient to remove the salt solution from the ion exchanger and the salt content was under 100 mg Cl^- per litre.

In Table III some data are given also from the gravimetric and titrimetric analysis of sulfate determinations without and with removal of the total hardness: the agreement is good.

It is convenient to standardize the solution so that 1 ml is equal to 1 mg SO_4^{-2}.

Reagents and solutions

3.9 grams of disodium dihydrogen ethylenediaminetetra-acetic acid (I.C.I.) are dissolved in sufficient water to make 1 litre of solution.

This solution was standardized against a calcium solution containing 1.042 g of pure calcium carbonate dissolved in hydrochloric acid and diluted to 1 litre in a volumetric flask, 1 ml of reagent is 1 mg SO_4^{-2}.

Ammonia-ammonium chloride buffer solution

10 grams of dipotassium magnesium ethylenediaminetetra-acetic acid (B. Siegfried, Zofingen, Switzerland) are dissolved in 200 ml of distilled water and added to a solution of 70 g ammonium chloride in 1800 ml of ammonia (25%).

Indicator solution

0.5 grams of eriochrome black T (Solochrome black W.D.F.A.) (I.C.I.) and 4.5 grams of hydroxylamine hydrochloric acid are dissolved in 100 ml of alcohol (96%).

Barium chloride solution

1.2 grams of $BaCl_2.2H_2O$ are dissolved in 1 litre of distilled water.

PROCEDURE

To 100.00 ml of totally softened water (see above) in an erlenmeyer flask are added 1 ml 2*N* HCl and 25.00 ml of barium chloride solution and boiled for five minutes.

This solution is kept warm overnight. After cooling 4 ml of the buffer solution and 7 drops of eriochrome black T are added and the solution is titrated at once with the standard ethylenediaminetetra-acetate solution to a pure blue endpoint.

The difference between the amount of titrant for 25.00 ml of barium chloride solution and the amount of titrant of the test, gives the number of milligrams of sulfate SO_4^{-2} in the water.

I am very much indebted to Mr. P. C. VAN VLIET for the analyses which he has carried out.

SUMMARY

Barium chloride is added to the sulfate and the excess determined by titration with the disodium salt of ethylenediaminetetra-acetic acid; hence the sulfate content is calculated.

The influence of time and temperature on the precipitation of barium sulfate has been studied. Calcium and magnesium ions are eliminated by ion exchangers.

RÉSUMÉ

L'auteur propose un dosage de sulfate par addition d'un excès de chlorure de baryum que l'on titre avec le sel de sodium de l'acide éthylènediaminotétracétique. L'influence du temps et de la température sur la précipitation du sulfate de baryum a été étudiée. Le calcium et le magnésium sont éliminés à l'aide d'échangeurs d'ions.

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ZUSAMMENFASSUNG

Es wird Bariumchlorid hinzugefügt und der Überschuss durch Titration mit dem Natriumsalz der Äthylendiamintetraesssigsäure bestimmt; danach wird der Sulfatgehalt berechnet. Es wurde der Einfluss der Zeit und der Temperatur auf die Ausfällung von Bariumsulfat untersucht. Calcium- und Magnesiumionen wurden durch Ionenaustauscher entfernt.

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DETERMINATION OF TIN IN TITANIUM ALLOYS

by

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INTRODUCTION

Because of the growing importance of tin-titanium alloys, this laboratory was called upon to develop a procedure for the determination of tin in this type of material. An attempt was made to determine the tin by direct iodometric titration. This was not successful due to interference from the titanium and such elements as chromium, tungsten and vanadium. It was decided that it would be necessary first to separate the tin from the titanium. Various separations were considered. The metastannic acid separation method[5] was not applicable because titanium precipitates with the tin. This was also true of the manganese dioxide separation method[7,8]. The distillation method for tin is troublesome, since it requires an all glass apparatus and a current of inert gas for good results[11]. The best separation for tin seemed to be the sulfide method. Experiments showed that more complete recovery of the tin was obtained when the tin sulfide was precipitated from a sulfuric rather than a hydrochloric acid solution. This was probably due to the fact that tin sulfide (both stannous and stannic) is more soluble in hydrochloric acid than in sulfuric acid[9]. More complete recovery of the tin was obtained when the titanium was in the oxidized state. This was probably due to the fact that stannous sulfide is more soluble than stannic sulfide[9]. If any titanium is present as the titanous ion, the tin can only be present in the stannous state. The best means for oxidizing the titanium was to add potassium permanganate. The excess permanganate was then destroyed by the addition of tartaric acid. If the permanganate were not destroyed, sulfur would form in the solution on treatment with hydrogen sulfide. The tartaric acid also prevents co-precipitation of vanadium sulfide with the tin sulfide.

Having selected the hydrogen sulfide method as a means of separating the tin, the next step was its actual determination. Considerable effort was expended in attempting to determine the tin colorimetrically. However, none of the commonly used reagents for tin, such as dithiol[2,14], molybdenum blue[1,15] or cacotheline[4,10] showed sufficient accuracy or precision. The best method for the determination of the tin seemed to be the iodometric titration. In the method as finally developed, the sulfide precipitate was dissolved in a mixture of sulfuric, perchloric and nitric acids, and the solution evaporated to fumes of sulfuric acid. The tin was then reduced with lead and antimony trichloride and titrated with iodine. A study was made of interfering elements that might be found in titanium alloys. It is stated in the literature[3,6,12,13] that such elements as molybdenum, tungsten, vanadium, chromium and copper interfere with the tin determination, but no definite data as to the extent of the interference seems available.

The method proposed in this paper is recommended for tin-titanium alloys containing 0.05 to 5.0 per cent. tin.

REAGENTS

Standard iodine solution (1 ml = approximately 0.0013 gram tin). Dissolve 5.0 grams of iodine and 50 grams of potassium iodide in 25 ml of water. Dilute to 2 liters with water. Standardize against Standard Tin Solution.

Standard tin solution (1 ml = 1.0 mg tin). Dissolve 1.0000 gram tin in 100 ml of hydrochloric acid, transfer to a 1 liter volumetric flask, cool and dilute to the mark with water.

Potassium permanganate solution (3 per cent.). Dissolve 30 grams of potassium permanganate in water and dilute to 1 liter with water.

Tartaric acid (20 per cent.). Dissolve 200 grams of tartaric acid in water and dilute to 1 liter with water.

Hydrogen sulfide wash solution. Add 10 ml of sulfuric acid to 1 liter of water and saturate with hydrogen sulfide.

Antimony trichloride solution (2 per cent.). Dissolve 10 grams of antimony trichloride in 250 ml of hydrochloric acid and dilute to 500 ml with water.

Potassium iodide solution (10 per cent.). Dissolve 10 grams of potassium iodide in water and dilute to 100 ml with water.

Starch solution (1 per cent.). Dissolve 1 gram of starch by boiling with about 80 ml of water. Cool and dilute to 100 ml with water.

Sodium carbonate solution (10 per cent.). Dissolve 200 grams of sodium carbonate in water and dilute to 2 liters with water.

RECOMMENDED PROCEDURE

Transfer a 1 gram sample to a 400 ml beaker and add 150 ml of water and 10 ml of sulfuric acid. Heat on the hot plate until the sample is dissolved. Remove from the hot plate. Add potassium permanganate solution (3 per cent.) until the solution is just about colorless due to the disappearance of the titanous color, then add sufficient permanganate to color the solution pink. Add 10 ml of tartaric acid (20 per cent.) and allow to stand for a few minutes to destroy the permanganate color. Add a little paper pulp and dilute to about 300 ml with water. Pass hydrogen sulfide through the solution for 15 minutes. Allow to stand overnight. Filter through a medium texture filter paper (Whatman No. 40) and wash with hydrogen sulfide wash solution. Place the filter paper and precipitate into a 500 ml Erlenmeyer flask containing 15 ml of sulfuric acid, 25 ml of nitric acid and 3 ml of perchloric acid. Evaporate to fumes to destroy the filter paper and continue heating for about 20 minutes at strong heat in order to drive off the perchloric acid. Allow to cool. Add 100 ml of water, 80 ml of hydrochloric acid, 1 ml of antimony trichloride solution (2 per cent.) and 8 grams of test lead. Dilute to about 300 ml with water and cover with a watch glass. Heat to boiling and boil for 30 minutes. Move the flask to the edge of the hot plate and attach a rubber stopper containing a capillary tube which dips to the bottom of a test tube filled with sodium carbonate solution (10 per cent.). Cool to about 10° C in an ice bath. Remove the stopper and add a mixture of 5 ml of potassium iodide solution (10 per cent.) and 5 ml of starch solution (1 per cent.). Titrate to a blue color with standard iodine solution from a burette whose tip passes through a 2-holed rubber stopper fitted into the neck of the flask.

Calculate the per cent. tin from the following formula:

$$\% \text{ Tin} = (A\text{-}B)\ C \times 100$$

A = ml of iodine solution required for titration
B = ml of iodine solution required for blank
C = tin equivalent of iodine solution in gram per ml

RESULTS AND DISCUSSION

The results obtained for tin in synthetic samples of tin-titanium alloys are shown in Table I.

The results obtained for tin in the presence of possible interfering elements

TABLE I

RESULTS FOR TIN IN SYNTHETIC SAMPLES OF TIN-TITANIUM ALLOYS

Tin present (%)	Tin found (%)	Std dev. (%)	No. of Determinations
0.050	0.054	0.012	5
0.50	0.50	0.016	5
1.00	0.99	0.013	6
2.50	2.51	0.012	5
5.00	5.00	0.029	5

are shown in Table II. No interference with the method was encountered from the amounts of these elements that would be expected to be found in commercial tin-titanium alloys. Molybdenum is quantitatively precipitated with the tin as the sulfide and it was found that the presence of more than 0.5 per cent. molybdenum

TABLE II

RESULTS FOR TIN IN THE PRESENCE OF POSSIBLE INTERFERENCES

Element	Amount added (%)	Added as	Tin present (%)	Tin found (%)
Molybdenum	2.5	$(NH_4)_6Mo_7O_{24}.4H_2O$	0.00	0.03
,,	1.0	,,	0.00	0.02
,,	0.5	,,	0.00	0.00
,,	1.0	,,	1.00	1.05
,,	0.5	,,	1.00	1.01
,,	1.0	,,	2.50	2.61
,,	0.5	,,	2.50	2.52
Tungsten	7.5	$Na_2WO_4.2H_2O$	0.00	0.00
,,	10.0	,,	0.00	0.00
,,	10.0	,,	1.00	1.01
,,	10.0	,,	2.50	2.49
Vanadium	10.0	$(VO)_2Cl_4$	0.00	0.00
,,	10.0	,,	1.00	0.99
,,	10.0	,,	2.50	2.49
Chromium	10.0	$Cr_2(SO_4)_3$	1.00	1.00
,,	10.0	,,	2.50	2.48
Silicon	5.0	$Na_2SiO_3.9H_2O$	1.00	1.01
Copper	1.0	$CuSO_4.5H_2O$	0.00	0.00
,,	0.2	,,	1.00	1.01
,,	0.5	,,	1.00	1.00
,,	0.9	,,	1.00	1.00
,,	1.0	,,	1.00	0.98
,,	2.5	,,	1.00	0.27
,,	5.0	,,	1.00	0.10
Iron	10.0	Metallic Iron	1.00	0.99
,,	10.0	,,	2.50	2.48
Aluminum	10.0	$Al_2(SO_4)_3.18H_2O$	1.00	1.01
Manganese	10.0	$MnSO_4.H_2O$	1.00	1.00
Nickel	10.0	$NiCl_2.6H_2O$	1.00	1.00
Cobalt	10.0	$CoCl_2.6H_2O$	1.00	0.99
Phosphorus	1.0	$(NH_4)_2HPO_4$	1.00	1.01
Boron	1.0	H_3BO_3	1.00	0.98

causes high results for tin. For samples containing larger amounts of molybdenum the interference of molybdenum could be eliminated by making an ammoniacal precipitation of the tin in the presence of iron following the fuming with sulfuric

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acid. Ten per cent. tungsten does not interfere with the method. Only a portion of the tungsten present in the sample is precipitated as insoluble tungstic acid because of the solvent action of titanium salts on tungstic acid. Vanadium and chromium do not interfere with the method because they are separated by the sulfide precipitation. If they were not removed, they would interfere because they would be partially reduced and titrated. The presence of more than 0.9 per cent. copper causes low results for tin. These low results are produced because the tin is partially precipitated as a copper-tin alloy[3,6,] and because the cupric copper left in solution reacts with the potassium iodide to give iodine which oxidizes the stannous tin[6,12]. It has been stated[3,8] that the presence of antimony trichloride reduces interference of copper with the tin determination because of the precipitation of a copper-antimony alloy in preference to the copper-tin alloy. However, no data has been given as to the extent of the elimination of the copper interference by the antimony, nor has the optimum amount of antimony been fully established. A study was made in this laboratory of the effect of antimony trichloride in reducing the interference of copper with the tin determination. The results obtained are shown in Table III. The optimum amount of antimony trichloride solution (2 per cent.) is 1 or 2 ml. There is a tendency towards low results when more than 3 ml of antimony trichloride solution are used. This tendency could be due to the difficulty of detecting the end-point against the background of suspended antimony.

TABLE III

EFFECT OF AMOUNT OF ANTIMONY TRICHLORIDE ON INTERFERENCE OF COPPER WITH TIN DETERMINATION
(1 per cent. tin and 1 per cent. copper present)

ml Antimony trichloride solution (2%)	Tin found (%)
0	0.35
0.1	0.51
0.5	0.75
1.0	0.98
2.0	0.98
3.0	0.97
5.0	0.96
10.0	0.96
25.0	0.96

The effect of the boiling time used in reducing the tin (counted from the moment the solution started to boil) is shown in Table IV. Twenty to thirty minutes are recommended. It is to be noted that there is no danger of volatilizing the tin even when the solution is boiled for 2 hours.

TABLE IV

EFFECT OF BOILING TIME USED IN REDUCING THE TIN
(2.50 per cent. tin present)

Time of boiling (Min)	Results for tin (%)
1	0.24
5	2.15
10	2.51
15	2.52
20	2.52
30	2.52
60	2.50
90	2.51
120	2.50

SUMMARY

Tin-titanium alloys are becoming increasingly important; consequently a good method is needed for the determination of tin in this type of material. In this paper an accurate iodometric procedure is proposed for the determination. The sample is dissolved in sulfuric acid and the titanium oxidized with potassium permanganate. Tartaric acid is added and the tin precipitated with hydrogen sulfide. The sulfide precipitate is dissolved in a mixture of sulfuric, perchloric and nitric acids and the solution evaporated to fumes of sulfuric acid. Water and hydrochloric acid are added, and the tin is reduced with lead and antimony trichloride and titrated with iodine. A study was made of the interfering elements that might be found in titanium alloys. The effect of antimony trichloride in reducing interference from copper was investigated. The method is recommended for titanium alloys containing 0.05 to 5.0 per cent. tin.

RÉSUMÉ

Les alliages étain-titane deviennent de plus en plus importants. C'est pourquoi une bonne méthode est nécessaire pour le dosage de l'étain dans ces alliages. Dans cet article, les auteurs proposent une méthode iodométrique. L'échantillon est dissous dans l'acide sulfurique et le titane est oxydé par le permanganate de potassium. On ajoute de l'acide tartrique; l'étain est précipité avec l'hydrogène sulfuré. Le sulfure formé est dissous dans un mélange d'acides sulfurique, perchlorique et nitrique; la solution est ensuite évaporée jusqu'à formation de vapeurs d'acide sulfurique. On ajoute de l'eau et de l'acide chlorhydrique; l'étain est réduit par le plomb et le trichlorure d'antimoine, et titré par l'iode. L'influence des éléments pouvant se rencontrer dans ces alliages de titane a été examinée. L'effet du trichlorure d'antimoine sur le cuivre a été également étudié. Cette méthode peut être recommandée pour des alliages de titane renfermant de 0.05 à 5.0% d'étain.

ZUSAMMENFASSUNG

Zinn-Titan-Legierungen gewinnen zunehmend an Bedeutung; es ist folglich eine gute Bestimmungsmethode für Zinn in dieser Art von Legierung notwendig. In dieser Arbeit wird ein genaues jodometrisches Bestimmungsverfahren vorgeschlagen. Die Probe wird in Schwefelsäure gelöst und Titan mit Kaliumpermanganat oxydiert. Weinsäure wird hinzugefügt und das Zinn mit Schwefelwasserstoff ausgefällt. Der Sulfidniederschlag wird in einer Mischung von Schwefel-, Überchlor- und Salpetersäure gelöst und die Lösung eingedampft bis die Schwefelsäure zu

rauchen beginnt. Dann wird Wasser und Salzsäure hinzugefügt und das Zinn mit Blei und Antimontrichlorid reduziert und mit Jod titriert. Es wurde eine Untersuchung der störenden Elemente durchgeführt, die in Titanlegierungen vorhanden sein können. Die Wirkung von Antimontrichlorid auf die Herabsetzung der von Kupfer verursachten Störung wurde untersucht. Die Methode wird für Titanlegierungen, die 0.05-5% Zinn enthalten empfohlen.

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THE DETERMINATION OF NITROGEN IN COPPER-TITANIUM ALLOYS

by

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INTRODUCTION

Nitrogen is present in many metals, both in the combined form and as adsorbed or entrapped gas. Nitride nitrogen is of considerable importance in copper-titanium alloys because of its embrittling effect upon the metal.

Wet chemical methods for the determination of nitrogen in metals and alloys have been used extensively. In many cases, results obtained by vacuum fusion techniques have been comparable to wet chemical procedures[5,14]. MALLET[11] employs the vacuum fusion method for determining nitrogen in copper. However, vacuum fusion methods have not proved entirely satisfactory for the determination of nitrogen in all metals. Furthermore, the apparatus necessary is expensive and is not available in many laboratories. Several investigators have reported satisfactory recoveries of nitrogen in steels by modified Kjeldahl procedures in which dilute sulfuric or hydrochloric acid is used for solution of the metal[1,9,17]. MASSINON[13] treats nitrides in cast iron by dissolving the metal in dilute sulfuric acid and separating the insoluble materials, such as the more refractory nitrides of titanium and vanadium. These refractory nitrides are then digested with hot concentrated sulfuric acid and potassium bisulfate. The use of small additions of hydrogen peroxide and hydrofluoric acid for the decompoposition of nitrides in steels and titanium alloys using dilute acid has been reported[5,19]. Similar digestion procedures have been used for magnesium and nickel-chromium alloys[2,14]. REDMOND, GERST AND TOUHEY[18] determined nitrogen in refractory metal carbides using sulfuric acid and potassium bisulfate to digest the sample. Although a very long digestion period is required for complete decomposition of the sample, the method has been successfully used for the analysis of titanium nitride.

Copper-titanium alloys are difficultly soluble in hot concentrated sulfuric acid. Attempts to increase the solvent effect of sulfuric acid by additions of potassium sulfate to raise the boiling point were successful, but care must be observed to prevent the mixture from approaching the composition of potassium bisulfate by loss of acid upon prolonged fuming.

Many investigators report that the use of perchloric acid as an oxidant in Kjeldahl digestion mixtures leads to considerable loss of nitrogen. HAGUE, PAULSON AND BRIGHT[5] abandoned experiments with perchloric acid for the decomposition of acid-insoluble nitrides in steel. These authors note that the duration of the fuming period markedly affected the magnitude of nitrogen losses. WICKS AND FIRMINGER[20] claim that the use of perchloric acid to accelerate the decomposition of organic materials in Kjeldahl digestion mixtures causes loss of nitrogen due to oxidation, or the formation and subsequent decomposition of ammonium perchlorate. These findings are supported by others[7,15]. All of these methods, however, report the use of small additions of perchloric acid to mixtures of sulfuric acid and salt followed by fuming for various lengths of time. Other analysts, working with organic samples, used small amounts of perchloric acid in sulfuric acid mixtures and reported quantitative recoveries provided the reagent is added in sufficient quantity to just clear the digestion mixture and the subsequent heating is very gentle[4,10,12,16]. KIRK[8] states that the use of a strong oxidizing agent is considered safe only when there is present an excess of other reducing agents which will be oxidized in preference to ammonia.

Perchloric acid does not act as a powerful oxidizing agent unless it is hot and concentrated. It is obvious that the important conditions necessary for the digestion of copper-titanium alloys with perchloric acid involve:

(1) An oxidizing attack in order to attain solution of the alloy within a reasonable time interval;

(2) Careful regulation of temperature and concentration of perchloric acid in order to avoid intensified oxidizing conditions;

(3) The presence of a reducing agent which will be preferentially oxidized during fixation of nitride nitrogen.

The method proposed in this paper requires the use of 5 ml of 70 per cent. perchloric acid to dissolve 0.5 to 1.5 g of copper alloy containing up to ten per cent. titanium. The digestion is carried out by carefully heating to barely perceptible fumes. The reaction is stopped shortly after all the sample has been decomposed, thus insuring an excess of reducing agent during the decomposition.

An individual analysis can be completed in 25 to 30 minutes.

APPARATUS AND REAGENTS

A Parnas-Wagner micro-Kjeldahl distillation apparatus.

Micro-burette, 5 ml capacity having 0.01 ml subdivisions.

References p. 46/47.

Perchloric acid, 70 to 72 per cent.

Sodium hydroxide, 30 per cent. solution. Add 700 ml water to 300 grams of cp sodium hydroxide pellets.

Boric acid solution, 2 per cent. Dissolve 20 grams of cp boric acid powder in 400 ml warm water and dilute to 1000 ml with water.

Indicator solution. Dissolve 0.1 gram of brom cresol green in 100 ml of 95 per cent. alcohol. Dissolve 0.1 gram of methyl red in 100 ml of 95 per cent. alcohol. Mix two parts methyl red and 1 part brom cresol green for use.

Hydrochloric acid 0.01*N*, approximately. Dilute 1 ml of cp hydrochloric acid (sp. gr. 1.18) to one liter in a volumetric flask and standardize as follows: Transfer 0.08 gram of National Bureau of Standards Borax, $Na_2B_4O_7.10H_2O$ into a 125 ml Erlenmeyer flask. Dissolve in 10 ml of freshly boiled water. Add 2 drops of mixed indicator and titrate while still hot, using a 50 ml burette.

$$\text{Normality} = \frac{\text{Wt Borax}}{\text{ml HCl} \times 0.19076}$$

EXPERIMENTAL

Due to the lack of standard copper-titanium alloys, an alloy of known nitrogen content containing approximately 10 per cent. titanium and 90 per cent. copper was carefully prepared.

Finely divided titanium sponge (100 mesh) was placed in a porcelain tube and heated for 15 minutes at 900° C in an atmosphere of nitrogen. The bronze colored titanium nitride obtained in this manner was analyzed, using the digestion procedure of REDMOND, GERST AND TOUHEY[18], in which a one-gram sample is decomposed by heating with sulfuric acid and potassium bisulfate. The nitrogen content was found to be 8.76 per cent.

A weighed portion of this substance was used in the casting of the standard alloy. The casting was done in an atmosphere of pure argon. Fine millings of this alloy were used for developmental work.

Preliminary experiments were conducted in order to ascertain the practicability of adapting established Kjeldahl digestion techniques to this determination.

Samples of the standard alloy (0.5 g) were placed in 50 ml Kjeldahl digestion flasks. Five ml of concentrated sulfuric acid and 3 grams of potassium sulfate were added to each flask. The samples did not completely dissolve even after 8 hours of boiling. Control samples, to which were added small quantities of ammonium sulfate, were simultaneously carried through the same procedure. Nitrogen recoveries in these control samples were somewhat low and erratic.

This procedure was repeated using 7.5 grams of potassium sulfate in 5 ml of concentrated sulfuric acid with alloy samples. Although complete decomposition of the sample was effected in 3 to 4 hours, substantial losses of nitrogen occurred in these samples and in ammonium sulfate standard samples which were carried through the same procedure as a control.

A standard micro-Kjeldahl digestion oven equipped with micro burners was used for uniform heating of these mixtures.

The composition of potassium bisulfate should never be approached in Kjeldahl digestion mixtures. KIRK[8] states that nitrogen is lost quantitatively if the ratio of potassium sulfate to sulfuric acid becomes too high. Upon prolonged fuming, sufficient sulfuric acid may be lost by volatilization to form a mixture approaching the composition of potassium bisulfate. This phenomenon may well be the cause of the serious losses of nitrogen which resulted.

It was evident that a more efficient means of dissolving these alloys was essential. The effect of oxidizing acids upon copper is recognized. Attention was therefore given to the possible use of perchloric acid in this procedure. COHN[3] proposed the use of this reagent as a digestion medium for the decomposition of small amounts of refractory nitrides found in pig iron. This author experimented with additions of ammonium sulfate and ammonium chloride in 60 per cent. perchloric acid. Quantitative recovery of nitrogen was claimed even after the samples were fumed to dryness. JOHNSON[6] used perchloric acid to digest insoluble nitrides in steels. KAYE AND WEINER[7] suggest that losses might occur before fixation of nitrogen when perchloric acid is used as an aid in the decomposition of organic materials.

To determine the extent of nitrogen losses, if any, using perchloric acid as a digestion medium, exactly 0.5 gram of standard copper-titanium alloy and 5 ml of 72 per cent. perchloric acid were placed in a 50 ml Erlenmeyer flask. Control samples were prepared in the same manner using measured amounts of standard $0.02N$ ammonium hydroxide solution. These samples were heated gently to fumes on a warm hot plate and allowed to fume lightly for a half hour with occasional swirling.

This operation was repeated with gentle fuming for one hour (about four times the period necessary to dissolve an 0.5 gram sample).

Other sets of samples were similarly prepared and fumed strongly enough to permit the vapors of perchloric acid to reflux, but not to reach the top of the flask.

Quantitative recovery was obtained in all cases with gentle fuming. The strongly heated samples showed that losses do occur due to either oxidation of ammonia or to volatilization of ammonium salts or a possible combination of these phenomena.

PROCEDURE

Transfer a 0.5 to 1.5 g sample of chips or drillings into a 50 ml Erlenmeyer flask. Add exactly 5 ml of 70 to 72 per cent. perchloric acid, measured from a pipette, and 1 to 2 ml of distilled water. Place on a warm hot plate and heat to gentle boiling with occasional swirling. As the water evaporates and the acid concentration increases, decomposition of the alloy becomes more rapid. Fume very lightly, with occasional swirling of the contents of the flask. Complete decomposition is obtained when particles of alloy are no longer present, and either a clear solution or a fine deposit of hydrolyzed titanium can be seen through the bottom of the flask. Complete decomposition is accomplished within thirty minutes.

Remove the flask from the hot plate and cool under cold running water. Cautiously add 5 ml of distilled water and heat to boiling for a few seconds. Cool the mixture to room temperature.

The micro-Kjeldahl apparatus (Fig. 1) should be thoroughly steamed out for a half hour prior to the first determination. Transfer the sample into the distillation flask through funnel (D) using a minimum of wash water for the transfer. Slowly add 10 to 15 ml of 30 per cent. sodium hydroxide. Close the clamp (H). Place a 125 ml Erlenmeyer flask containing 10 ml of boric acid solution and 2 drops of the mixed indicator on the support so that the tip of the condenser is immersed in the solution.

With (G) open, apply heat to (B) until steam issues freely from (G). Close (G) carefully. The distillation should be complete in 4 to 5 minutes after the silver tube condenser becomes hot at the top, or after 15 to 20 ml of distillate is collected.

Lower the receiving flask and collect the distillate for one minute longer. Wash the condenser tip with a stream of distilled water. Titrate the distillate to a definite pink end-point. A

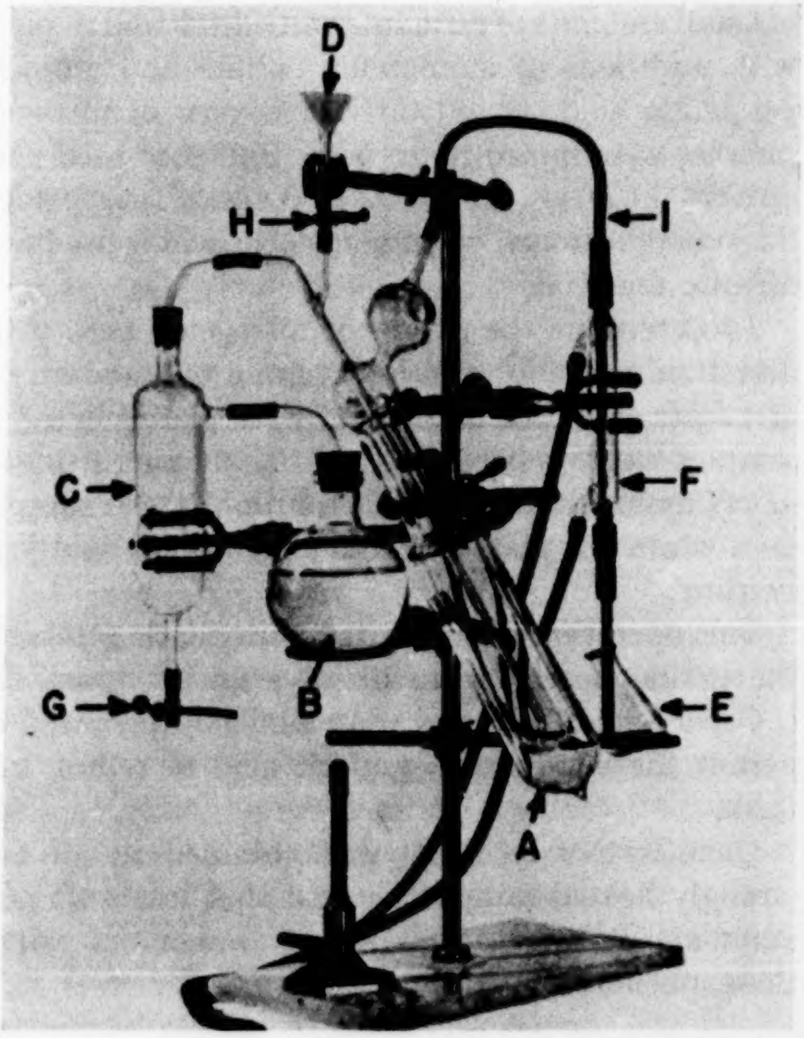

Fig. 1. Parnas and Wagner micro-Kjeldahl distillation apparatus.

References p. 46/47.

blank is run with the sample using 5 ml of perchloric acid and 15 ml of 30 per cent. sodium hydroxide solution.

Calculations:

$$\%\ \text{Nitrogen} = \frac{1.4\,(R-S)N}{W}$$

R = ml of standard acid used for sample
S = ml of standard acid used for blank
W = weight of sample (grams)
N = normality of standard acid

RESULTS

The results shown in Table I demonstrate the accuracy and precision of the method. Data are tabulated showing recoveries of nitride nitrogen in copper-titanium alloys (A) and of ammonia added as a standard solution of 0.02N ammonium hydroxide (B).

TABLE I

NITROGEN RECOVERY IN 5 ml OF 72 PER CENT. PERCHLORIC ACID

(A) Nitrogen in copper-titanium alloy

Sample size (g)	Nitrogen present (%)	Period of fuming (hr)	Manner of fuming	Nitrogen found (%) (Avg)	No. of determinations	Standard deviation (%)
0.5000	0.136	½	Light	0.137	12	0.0020
1.0000	0.136	½	Light	0.136	5	0.0027
0.5000	0.136	1	Light	0.135	6	0.0031
0.5000	0.136	½	Strong	0.132	5	0.0017
0.5000	0.136	1	Strong	0.126	5	0.0024

(B) Nitrogen added as 0.02N ammonium hydroxide solution

Nitrogen present (mg)	Period of fuming (hr)	Manner of fuming	Nitrogen found (mg) (Avg)	No. of determinations	Standard deviation (mg)
0.521	½	Light	0.523	5	0.0018
0.521	1	Light	0.523	5	0.0019
0.521	½	Strong	0.463	5	0.0244
0.521	1	Strong	0.396	5	0.0520

SUMMARY

An experimental program on the casting of copper-titanium alloys is being conducted in this laboratory. It was suspected that nitrogen was absorbed from the atmosphere during these casting operations and possibly caused embrittlement of these alloys. An accurate means of determining nitrogen in copper-titanium alloys was therefore necessary. A rapid and accurate method is proposed for determining nitrogen in copper-titanium alloys which is satisfactory for quantities of nitrogen as low as 0.01 per cent. In the development of the procedure, a study was made of possible digestion solutions. A moderately concentrated solution of perchloric acid was found to be most practical for decomposing the sample. When solution of the sample is completed, the mixture is transferred to the flask of a micro-Kjeldahl distillation apparatus. Sodium hydroxide is added until the solution is distinctly alkaline, and the liberated ammonia is steam distilled into a solution of boric acid and titrated with standard acid.

RÉSUMÉ

Une étude expérimentale sur la fonte des alliages cuivre-titane a été effectuée dans ce laboratoire. On suppose que l'azote de l'atmosphère peut être absorbé pendant ces opérations en rendant ces alliages cassants. C'est pourquoi un dosage précis de l'azote dans les alliages cuivre-titane est nécessaire. Une méthode rapide et précise est proposée permettant de doser jusqu'à 0.01% d'azote. Les auteurs ont étudié également la mise en solution des échantillons, ils proposent d'utiliser l'acide perchlorique en solution modérément concentrée. Lorsque la dissolution est terminée, la solution est transvasée dans un appareil à distiller, de microkjeldahl. On ajoute de l'hydroxyde de sodium jusqu'à réaction nettement alcaline, l'ammoniac libéré est entraîné à la vapeur dans une solution d'acide borique et titré avec un acide étalon.

ZUSAMMENFASSUNG

Ein experimentelles Programm über das Giessen von Kupfer-Titan-Legierungen wurde in diesem Laboratorium durchgeführt. Es wurde vermutet, dass während des Giessverfahrens Stickstoff aus der Atmosphäre absorbiert wurde und möglicherweise ein Brüchigwerden dieser Legierungen verursachte. Ein genauer Weg zur Bestimmung von Stickstoff in Kupfer-Titan-Legierungen war daher notwendig. Eine schnelle und genaue Methode wird zur Bestimmung von Stickstoff in Kupfer-Titan-Legierungen vorgeschlagen, die befriedigende Werte bis zu einer Stickstoffmenge von 0.01% gibt. Bei der Entwicklung des Verfahrens wurde eine Untersuchung über mögliche Digerierungslösungen durchgeführt. Eine mässig konzentrierte Lösung von Überchlorsäure wurde als am meisten praktisch zur Zersetzung der Probe befunden. Ist die Auflösung der Probe vollständig, dann wird die Mischung in den Kolben einer Mikro-Kjeldahldestillationsapparatur übergebracht, Natriumhydroxyd wird hinzugefügt bis die Lösung deutlich alkalisch ist und das freigesetzte Ammoniak mit Dampf in eine Lösung von Borsäure destilliert und mit einer Säure von bekannten Titer titriert.

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THE ANALYSIS OF COMBUSTION PRODUCTS

III. THE EFFECT OF HYDROGEN PEROXIDE ON THE REACTION OF POTASSIUM PERMANGANATE WITH ORGANIC PEROXIDES IN ACID SOLUTION

by

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In the course of combustion research, the problem of the estimation of lower organic peroxides in the presence of hydrogen peroxide constantly arises. Although the present communication does not present a complete solution of the problem, it is felt that the observations will be relevant not only to those concerned with the analysis of combustion products, but also to those interested in electron transfer reactions involving peroxides.

It has been known for some time (RIECHE[1]) that, unlike hydrogen peroxide, neither methyl hydroperoxide nor ethyl hydroperoxide in acid solution react with potassium permanganate at room temperature. This difference between the behaviours of the organic peroxides and hydrogen peroxide should have provided a means of estimating the hydrogen peroxide content in a mixture of organic peroxides and hydrogen peroxide. The basis of the method was to have been an iodometric determination of total peroxide, together with a potassium permanganate titration of the hydrogen peroxide only. In fact, it was found that in acid solution, hydrogen peroxide brings about a reaction between methyl or ethyl hydroperoxide and potassium permanganate and consequently the failure of the previously suggested method of analysis.

Nevertheless, the investigation of the conditions under which hydrogen peroxide induces the reaction of methyl and ethyl hydroperoxides with potassium permanganate has given indications that a rapid empirical method for the determination of these peroxides can be achieved. In the presence of sufficient hydrogen peroxide, the difference between the total permanganate titre and that due to hydrogen peroxide was in fact proportional to the initial concentration of organic peroxide, and almost independent of that of the added hydrogen peroxide. The deduced equivalent of the organic peroxide was, however, much less than usual.

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These organic peroxides can react alone with acid potassium permanganate, but only on heating to approximately 70° C. The end-points are then rather indefinite, and losses occur due to evaporation.

EXPERIMENTAL

Methyl hydroperoxide and ethyl hydroperoxide were prepared by the action of methyl or ethyl sulphate on hydrogen peroxide; the method is described in detail elsewhere[2]. Aqueous solutions of known concentration were prepared from the pure materials by weighing.

Hydrogen peroxide was used as supplied by Messrs. Laporte and contained no stabiliser.

PROCEDURE

All the titrations were carried out in the presence of 25ml of 2*N* sulphuric acid. A known volume of organic peroxide solution was added to the sulphuric acid, followed by a known volume of freshly standardised hydrogen peroxide solution. The mixture was then titrated against potassium permanganate (0.002*M*) in the usual manner. The equivalent of the hydrogen peroxide present in ml of potassium permanganate was subtracted from the total titre to give the volume of permanganate corresponding to the organic peroxide.

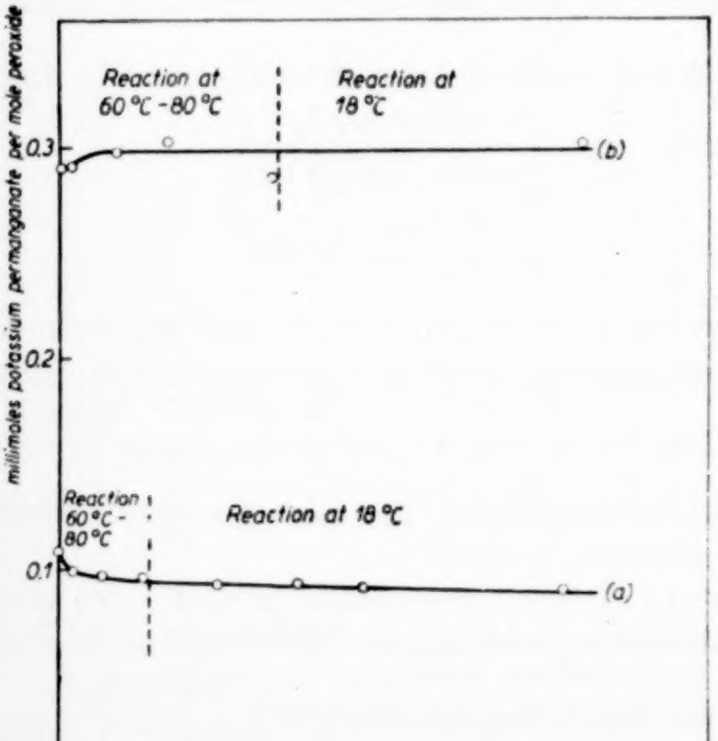

Fig. 1. The effect of hydrogen peroxide on the reaction of organic peroxides with potassium permanganate in acid solution.

(a) 0.221 m*M* of methyl hydroperoxide.
(b) 0.226 m*M* of ethyl hydroperoxide.

Hydrogen peroxide had a similar effect on the reaction of both organic peroxides with potassium permanganate. It is evident from Fig. 1 that a certain minimum quantity of hydrogen peroxide is required before the reaction will proceed at room temperature. The permanganate consumed by the peroxides was only slightly dependent on the amount of hydrogen peroxide present.

It can be seen from Fig. 1 (a) that for methyl hydroperoxide the ratio $\left(\frac{\text{moles } H_2O_2}{\text{moles } CH_3OOH}\right)$

must exceed about 0.25 for the reaction to occur at room temperature, whereas ethyl hydroperoxide requires rather more hydrogen peroxide, the corresponding ratio being about 0.5. As the amount of hydrogen peroxide is increased beyond these limits the quantity of permanganate used up by the methyl hydroperoxide falls slightly (from 0.0924 to 0.0888 mole permanganate/mole methyl hydroperoxide for an increase in the ratio $\left(\frac{\text{mole } H_2O_2}{\text{mole } CH_3OOH}\right)$ from 0.25 to 1.0).

For ethyl hydroperoxide the evidence (Fig. 1b) for a corresponding fall is less certain since at the lower ratios of $\left(\frac{H_2O_2}{C_2H_5OOH}\right)$ the reaction is somewhat sluggish and the end-point less precise.

When less hydrogen peroxide is present than is required by the above ratio, the reaction of both the organic peroxides only proceeds at temperatures rising to 60° C to 80° C, and for methyl hydroperoxide there is an increase in the permanganate used up, *i.e.* from $\left(\frac{\text{moles } CH_3OOH}{\text{moles } KMnO_4}\right) = 0.0924$ to 0.108 for a fall in $\left(\frac{\text{moles } H_2O_2}{\text{moles } CH_3OOH}\right)$ from 0.5 to 0. As stated previously the corresponding experiments with ethyl hydroperoxide did not indicate any definite trend in the permanganate used up on varying the ratio $\left(\frac{\text{moles } H_2O_2}{\text{moles } C_2H_5OOH}\right)$

The effect of organic peroxide

For this set of experiments the quantity of hydrogen peroxide was maintained constant and the quantity of organic peroxide present was varied, the ratio $\left(\frac{\text{moles } H_2O_2}{\text{moles } CH_3OOH}\right)$ being maintained at > 1. For an eightfold change in the quantity of methyl hydroperoxide the permanganate titre closely approximated to a linear function of the organic peroxide present.

For a tenfold change in the amount of ethyl hydroperoxide present there was again a practically linear relationship between permanganate titre and the amount of ethyl hydroperoxide present. For all except the last run the $\frac{\text{moles } H_2O_2}{\text{moles } C_2H_5OOH}$ ratio was greater than 0.5.

DISCUSSION

From the slope of the lines shown in Fig. 2 it is clear that, under these conditions of promotion by hydrogen peroxide, one mole of methyl hydroperoxide reacts with 0.093 moles potassium permanganate, whereas one mole of ethyl hydroperoxide reacts with 0.297 moles of potassium permanganate. It is possible that the true values of these figures are 0.1 and 0.3 respectively, the discrepancy being partially due to the difficulty in preparing highly pure samples of organic peroxides. The above figures are of interest inasmuch as they indicate that the overall reaction is complex, different for each peroxide, and cannot be expressed by the formal equation:

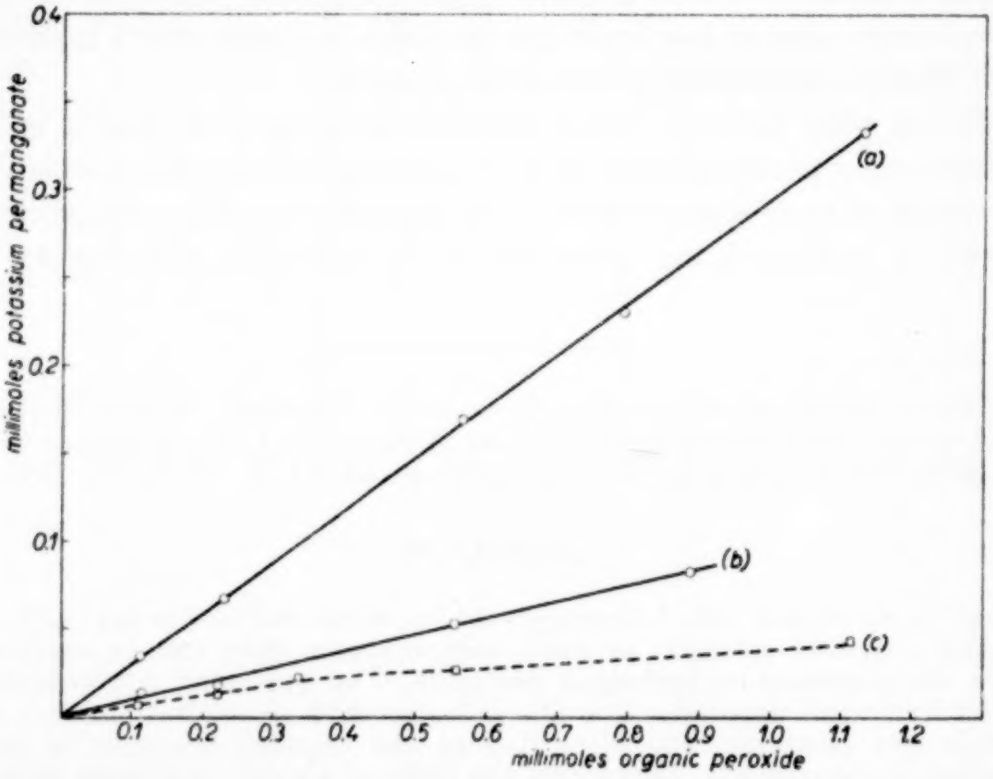

Fig. 2. The relationship between quantity of organic peroxide and equivalent amount of potassium permanganate.

a) ethyl hydroperoxide in the presence of 0.484 mM hydrogen peroxide.
b) methyl hydroperoxide in the presence of 0.914 mM hydrogen peroxide.
c) ethyl alcohol in the presence of 0.68 mM hydrogen peroxide.

$$2KMnO_4 + 5ROOH + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5ROH + 2H_2O + 5O_2.$$

A formaldehyde catalysed decomposition of the type described by RIECHE[1] and WEILAND[3] is probably not responsible for the low equivalent of methyl hydroperoxide, since, under our conditions, the addition of formaldehyde has no influence. It is also relevant that under our conditions hydrogen peroxide does not promote the reaction of formaldehyde with potassium permanganate in acid solution. Similarly, methanol is not attacked by potassium permanganate in the presence of hydrogen peroxide in acid solution. Ethanol, however, does react in a manner similar to that of ethyl hydroperoxide. Fig. 2 shows the result of an experiment in which ethanol in the presence of hydrogen peroxide was titrated against potassium permanganate at room temperature. From the initial section of the curve it is found that one mole of ethanol reacts with approximately 0.05 mole of potassium permanganate. The end-point is indefinite and is followed by a further slow reaction which is accelerated by heat.

The difference in the equivalents of methyl and ethyl hydroperoxide may in part be related to the differences in behaviour of the alcohols. This may be further accentuated by the ethanol induced oxidation of methanol by potassium permanganate in acid solution. The sluggishness and indefinite end-point of the reaction of ethyl hydroperoxide at low hydrogen peroxide concentrations is strongly reminiscent of the corresponding reaction of ethanol.

Experiments with tertiary butyl hydroperoxide showed that it is unreactive towards potassium permanganate in acid solution and that no reaction is induced by the presence of hydrogen peroxide. This suggests that the method can probably be adapted to remove lower peroxides from mixtures with higher peroxides.

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SUMMARY

Although methyl and ethyl hydroperoxides alone do not react with potassium permanganate in acid solution at room temperature, they can be oxidised by this reagent in the presence of hydrogen peroxide. The apparent equivalents (as compared with hydrogen peroxide) are much lower than usual but, in the presence of excess hydrogen peroxide, the titre due to the organic peroxide is proportional to its original concentration. This forms the basis of a simple titration method which, though empirical, is both rapid and accurate. Since *t*-butyl hydroperoxide does not react in this way, it may be possible to differentiate the higher peroxides from lower peroxides.

RÉSUMÉ

Les méthyl- et éthylhydroperoxydes ne réagissent pas avec le permanganate de potassium, en solution acide, à la température ordinaire, mais ils peuvent être oxydés par ce réactif en présence de peroxyde d'hydrogène. Les équivalents apparents, comparativement au peroxyde d'hydrogène, sont beaucoup plus faibles que normalement, mais en présence d'un excès de peroxyde d'hydrogène, le titre dû au peroxyde organique est proportionnel à sa concentration. Ceci est à la base d'une méthode de titration simple qui bien qu'empirique, est à la fois rapide et précise. Le *t*-butyl-hydroperoxyde ne réagit pas, dans ce cas: il peut être possible de différencier les peroxydes supérieurs des peroxydes inférieurs.

ZUSAMMENFASSUNG

Obwohl Methyl- und Äthylhydroperoxyde allein mit Kaliumpermanganat in saurer Lösung bei Zimmertemperatur nicht reagieren, können sie in Gegenwart von Wasserstoffsuperoxyd mit diesem Reagenz oxydiert werden. Die scheinbaren Äquivalente — verglichen mit Wasserstoffsuperoxyd — sind viel niedriger als

gewöhnlich, in Gegenwart eines Überschusses von Wasserstoffsuperoxyd aber ist der Titer für die organischen Peroxyde proportional zu ihrer ursprünglichen Konzentration. Dies bildet die Grundlage zu einer einfachen Titrationsmethode, die obwohl sie empirisch ist, schnell und genau ist. Da *t*-Butylhydroperoxyd so nicht reagiert ist es möglich höhere Peroxyde von niedrigeren Peroxyden zu unterscheiden.

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ESTIMATION OF METALS AS SULPHIDES

I. ESTIMATION OF BISMUTH, CADMIUM, LEAD, AND INDIUM

by

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In the earlier publications[1,2] from these laboratories it was shown that certain metals can be conveniently precipitated and estimated as sulphides by decomposing their thiosalts and weighing the precipitated sulphides after suitable treatment. This method was shown to be applicable to arsenic, selenium, tellurium, molybdenum, and tin.

The ease and accuracy with which these elements can be estimated as sulphides by decomposing the thiosalts showed that it might be possible to extend the method to those metals which do not form thiosalts but are precipitated completely as sulphides from acid or alkaline solutions. Although metals like bismuth, cadmium, lead, and indium form difficultly soluble sulphides their estimation as sulphide has not found much favour owing to certain difficulties encountered in precipitating them as sulphides from acid solutions.

A study of the behaviour of these metals with sodium and ammonium sulphides has shown that under proper conditions the metals can be precipitated and estimated as sulphides with remarkable ease and accuracy. This method is particularly useful in the case of bismuth and cadmium for which no entirely satisfactory and easy inorganic methods are available at present.

Materials. The most important of these is the alkali sulphide solution which is required for precipitating the element as sulphide. This is prepared from ammonium hydroxide or sodium hydroxide according to the method described earlier[3].

The other materials used in the various estimations were of B.D.H. AnalaR quality or Kahlbaum's. The solutions prepared from these materials were carefully standardized by well-known methods.

EXPERIMENTAL

Estimation of bismuth as Bi_2S_3

Bismuth is usually estimated as Bi_2O_3[4] after precipitation as carbonate or as BiOCl[5] when only a few milligrams of the metal are present in the solution.

The estimation of bismuth as Bi_2S_3[6] by passing hydrogen sulphide in hydrochloric or sulphuric acid solution, preferably under pressure, has also been recommended. None of these methods is entirely satisfactory and the following method of precipitating Bi_2S_3 by adding ammonium sulphide is simpler and the estimation takes about two hours. Sodium sulphide cannot be used for precipitating Bi_2S_3 on account of its solvent action on the precipitate.

A solution of bismuth chloride was prepared by dissolving bismuth carbonate (KAHLBAUM'S) in hydrochloric acid and standardized[7] by precipitating the metal as carbonate and igniting to Bi_2O_3. A measured volume of this solution was treated with ammonium hydroxide till a slight turbidity began to appear in the solution. It was then treated with an excess of freshly prepared ammonium sulphide reagent, the mixture was shaken thoroughly to ensure complete precipitation and the precipitate of Bi_2S_3 was filtered through a weighed Gooch crucible. The precipitate was washed thoroughly with hot water, dried at 105-115° C for about an hour and weighed as Bi_2S_3. The weights of metallic bismuth contained in the measured portion of the solution and those corresponding with the precipitate actually obtained are given in Tables I and II.

TABLE I

WITH CONCENTRATED AMMONIUM SULPHIDE REAGENT

No.	Vol. of bismuth solution in ml	Vol. of reagent added in ml	Wt. of ppt. Bi_2S_3 in g	Wt. of Bi in the ppt. in g	Wt. of Bi actually present in g
1	10	10	0.2368	0.1925	0.1925
	10	15	0.2366	0.1923	0.1925
	10	20	0.2368	0.1925	0.1925
2	20	10	0.4736	0.3850	0.3850
	20	15	0.4734	0.3849	0.3850
	20	20	0.4736	0.3850	0.3850
3	25	10	0.2960	0.2406	0.2406
	25	15	0.2958	0.2405	0.2406
	25	20	0.2958	0.2405	0.2406

Estimation of cadmium as CdS

It is well known that cadmium cannot be weighed as cadmium sulphide because the precipitate obtained by passing hydrogen sulphide in hydrochloric or sulphuric acid solution is not pure. The precipitate, after washing, is usually evaporated to dryness with sulphuric acid and the cadmium sulphate thus formed is then weighed. As the following procedure will show it is possible to precipitate cadmium as cadmium sulphide and to weigh it as such directly without the necessity of evaporating the precipitate with sulphuric acid provided we use

TABLE II

WITH 1N AMMONIUM SULPHIDE REAGENT

No.	Vol. of bismuth solution in ml	Vol. of reagent added in ml	Wt. of ppt. Bi_2S_3 in g	Wt. of Bi in the ppt. in g	Wt. of Bi actually present in g
1	10	10	0.2368	0.1925	0.1925
	10	15	0.2366	0.1923	0.1925
	10	20	0.2368	0.1925	0.1925
2	20	20	0.4732	0.3848	0.3850
	20	25	0.4732	0.3848	0.3850
	20	30	0.4734	0.3850	0.3850
3	25	15	0.2960	0.2406	0.2406
	25	20	0.2958	0.2405	0.2406
	25	25	0.2958	0.2405	0.2406

sodium sulphide (not ammonium sulphide) as the precipitating agent. The whole estimation can be completed in about two hours.

A solution of cadmium sulphate (AnalaR quality) was prepared and standardized[8] by precipitating as cadmium sulphide, evaporating with sulphuric acid and weighing the $CdSO_4$. Measured volumes of the solution were treated with excess of sodium sulphide solution to precipitate the cadmium as sulphide. The reagent should be added in small quantities at a time with constant shaking so that a granular precipitate with an orange colour may be obtained. If the reagent is added suddenly a yellow coloured precipitate is obtained and the results obtained under these conditions are too high. The precipitate of cadmium sulphide was filtered through a weighed Gooch crucible, washed thoroughly with moderately hot water, dried at 105-115° C for an hour and weighed as CdS. The weights of metallic cadmium obtained in the measured portions of the solution and those corresponding with the precipitate actually obtained are given in Table III.

TABLE III

WITH 2N SODIUM SULPHIDE REAGENT

No.	Vol. of cadmium solution in ml	Vol. of reagent added in ml	Wt. of ppt. CdS in g	Wt. of Cd in the ppt. in g	Wt. of Cd actually present in g
1	10	10	0.2126	0.1654	0.1654
	10	15	0.2125	0.1652	0.1654
	10	20	0.2126	0.1654	0.1654
2	20	10	0.1642	0.1277	0.1277
	20	15	0.1642	0.1277	0.1277
	20	20	0.1642	0.1277	0.1277
3	10	5	0.0821	0.06387	0.06387
	10	8	0.0821	0.06387	0.06387
	10	10	0.0820	0.06380	0.06387

References p. 61.

Estimation of lead as PbS

Lead is not usually estimated as sulphide for various reasons, the chief among them being slight oxidation of sulphide to sulphate and contamination of the precipitate with sulphur. A careful study of the conditions under which lead can be precipitated as sulphide has shown that the method of precipitation of sulphide by adding excess of alkali sulphide is applicable to this metal also provided the mixture is acidified with excess of acetic acid after adding the ammonium sulphide or sodium sulphide. The pure precipitate of PbS can be weighed directly and the whole estimation completed in two hours.

A solution of lead acetate was prepared with acetic acid and standardized by precipitation as $PbMoO_4$[9] or $PbCrO_4$[10]. Measured portions of this solution were treated with ammonium hydroxide till a slight turbidity appeared, then with excess of ammonium sulphide or sodium sulphide reagent. After the lead had been precipitated the mixture was acidified with 4*N* acetic acid. The acidified solution was heated to boiling, allowed to stand for about 10 minutes, filtered through a weighed sintered glass crucible (porosity 4). The precipitate was washed with cold water, alcohol and ether successively, sucked dry at the filter pump, dried in a vacuum desiccator for about half an hour and weighed as PbS. The weights of lead present in the solution and those corresponding to the precipitated lead sulphide are given below in Tables IV, V and VI and show excellent agreement.

Estimation of indium as In_2S_3

In the precipitation of indium sulphide[11] it is necessary to pass hydrogen sulphide for 2 hours at 70° C in a solution containing less than 0.05*N* hydrochloric acid or acetic acid. The precipitate has to be heated to 350° C in a stream of hydrogen sulphide and then cooled in the same.

The behaviour of indium salts with ammonium sulphide has shown that indium can be precipitated completely with far greater ease and accuracy if the solution containing indium is treated with freshly prepared ammonium sulphide. The mixture containing the precipitate may then be treated with acetic acid or with dilute hydrochloric acid (0.05*N*) to dissolve out other sulphides like those of manganese. In this way the lengthy procedure of passing hydrogen sulphide at a higher temperature is eliminated and the estimation can be completed in a much shorter time.

In studying the behaviour of indium with ammonium sulphide two sets of experiments were performed. In one set of experiments the solution containing the indium salt was treated with ammonium sulphide and the precipitate, after washing with hot water and drying, weighed as In_2S_3. In the other set of experiments the solution containing the indium salt was treated with ammonium sulphide and the mixture containing the precipitated sulphide was immediately acidified with acetic acid. The precipitate of In_2S_3 was then washed, dried and weighed. In both sets of experiments excellent results were obtained.

TABLE IV

WITH CONCENTRATED AMMONIUM SULPHIDE REAGENT FOLLOWED BY EXCESS OF 4*N* ACETIC ACID

No.	Vol. of Pb solution in ml	Vol. of reagent added in ml	Vol. of 4*N* acetic acid added in ml	Wt. of ppt. PbS in g	Wt. of Pb in the ppt. in g	Wt. of Pb actually present in g
1	10	10	45	0.1222	0.1059	0.1059
	10	15	60	0.1222	0.1059	0.1059
	10	20	80	0.1222	0.1059	0.1059
2	20	15	60	0.2443	0.2115	0.2116
	20	20	80	0.2444	0.2116	0.2116
	20	25	100	0.2444	0.2116	0.2116
3	25	10	45	0.1578	0.1367	0.1367
	25	15	60	0.1578	0.1367	0.1367
	25	20	80	0.1578	0.1367	0.1376

TABLE V

WITH 1*N* AMMONIUM SULPHIDE REAGENT FOLLOWED BY EXCESS OF 4*N* ACETIC ACID

No.	Vol. of Pb solution in ml	Vol. of reagent added in ml	Volume of 4*N* acetic acid added in ml	Wt. of ppt. PbS in g	Wt. of Pb in the ppt. in g	Wt. of Pb actually present in g
1	10	10	5	0.1222	0.1059	0.1059
	10	15	8	0.1222	0.1059	0.1059
	10	20	10	0.1222	0.1059	0.1059
2	20	20	10	0.2444	0.2116	0.2116
	20	25	10	0.2444	0.2116	0.2116
	20	30	10	0.2444	0.2116	0.2116
3	25	10	10	0.1578	0.1367	0.1367
	25	15	15	0.1578	0.1367	0.1367
	25	20	20	0.1578	0.1367	0.1367

TABLE VI

WITH 2*N* SODIUM SULPHIDE REAGENT FOLLOWED BY EXCESS OF 4*N* ACETIC ACID

No.	Vol. of Pb solution in ml	Vol. of reagent added in ml	Vol. of 4*N* acetic acid added in ml	Wt. of ppt. PbS in g	Wt. of Pb in the ppt. in g	Wt. of Pb actually present in g
1	10	10	10	0.1222	0.1059	0.1059
	10	15	10	0.1222	0.1059	0.1059
	10	20	15	0.1221	0.1058	0.1059
2	20	20	15	0.2444	0.2116	0.2116
	20	25	15	0.2443	0.2115	0.2116
	20	30	20	0.2444	0.2116	0.2116
3	25	10	10	0.1578	0.1367	0.1367
	25	15	15	0.1578	0.1367	0.1367
	25	20	20	0.1578	0.1367	0.1367

References p. 61.

A solution of indium chloride (KAHLBAUM's) was prepared and standardized[12] by precipitating the hydroxide and igniting the precipitate to In_2O_3. Measured portions of this solution were treated first with ammonium hydroxide solution to neutralize the hydrochloric acid until a slight turbidity appeared and then with an excess of ammonium sulphide to precipitate the In_2S_3. The yellowish-white precipitate was filtered through a weighed sintered glass crucible (porosity 4), washed with hot water, dried at 120-125° C for about an hour and weighed as In_2S_3. The precipitate turns yellow on washing and orange on drying. Sodium sulphide cannot be used for precipitating In_2S_3 as it has a solvent action on the precipitate.

In the experiments in which the sulphide mixture is finally acidified with acetic acid the mixture should be heated to boiling after acidification, allowed to stand for 15-20 minutes, and filtered under very low pressure, otherwise the precipitate tends to pass through the filter.

The weights of metallic indium contained in the measured portions of the solution and those corresponding with the precipitate actually obtained are given in Tables VII, VIII, IX and X.

TABLE VII

WITH CONCENTRATED AMMONIUM SULPHIDE REAGENT

No.	Vol. of In solution in ml	Vol. of reagent added in ml	Wt. of In_2S_3 ppt. in g	Wt. of In in the ppt in g	Wt. of In actually present in g
1	2	15	0.0292	0.02058	0.02058
	2	20	0.0292	0.02058	0.02058
	2	25	0.0292	0.02058	0.02058
2	5	15	0.0402	0.02834	0.02834
	5	20	0.0401	0.02827	0.02834
	5	25	0.0402	0.02834	0.02834
3	10	15	0.0974	0.06868	0.06869
	10	20	0.0974	0.06868	0.06869
	10	25	0.0974	0.06868	0.06869

TABLE VIII

WITH 1*N* AMMONIUM SULPHIDE REAGENT

No.	Vol. of In solution in ml	Vol. of reagent added in ml	Wt. of In_2S_3 ppt. in g	Wt. of In in the ppt. in g	Wt. of In actually present in g
1	2	10	0.0292	0.02058	0.02058
	2	15	0.0291	0.02052	0.02058
	2	20	0.0292	0.02058	0.02058
2	5	15	0.0402	0.02834	0.02834
	5	20	0.0402	0.02834	0.02834
	5	25	0.0402	0.02834	0.02834
3	10	15	0.0974	0.06868	0.06869
	10	20	0.0974	0.06868	0.06869
	10	25	0.0974	0.06868	0.06869

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TABLE IX

WITH CONCENTRATED AMMONIUM SULPHIDE REAGENT FOLLOWED BY EXCESS OF 5N ACETIC ACID

No.	Vol. of In solution in ml	Vol. of reagent added in ml	Vol. of 5N acetic acid added in ml	Wt. of ppt In_2S_3 in g	Wt. of In in the ppt. in g	Wt. of In actually present in g
1	2	15	50	0.0292	0.02058	0.02058
	2	20	60	0.0292	0.02058	0.02058
	2	25	80	0.0292	0.02058	0.02058
2	5	15	50	0.0402	0.02834	0.02834
	5	20	60	0.0401	0.02827	0.02834
	5	25	80	0.0402	0.02834	0.02834
3	10	15	60	0.0973	0.06860	0.06869
	10	20	80	0.0974	0.06868	0.06869
	10	25	100	0.0974	0.06868	0.06869

TABLE X

WITH 1N AMMONIUM SULPHIDE REAGENT FOLLOWED BY EXCESS OF 5N ACETIC ACID

No.	Vol. of In solution in ml	Vol. of reagent added in ml	Vol. of 5N acetic acid added in ml	Wt. of ppt. In_2S_3 in g	Wt. of In in the ppt in g	Wt. of In actually present in g
1	2	15	20	0.0292	0.02058	0.02058
	2	20	25	0.0292	0.02058	0.02058
	2	25	30	0.0292	0.02058	0.02058
2	5	15	25	0.0402	0.02834	0.02834
	5	20	30	0.0402	0.02834	0.02834
	5	25	35	0.0401	0.02827	0.02834
3	10	15	30	0.0974	0.06868	0.06869
	10	20	35	0.0974	0'06868	0.06869
	10	25	40	0.0974	0.06868	0.06869

SUMMARY

1. It has been shown that under proper conditions bismuth, cadmium, lead and indium can be precipitated quantitatively as pure sulphides by alkali sulphides and the precipitate weighed directly for the estimation of the metal.

2. In the case of bismuth ammonium sulphide gives a pure precipitate of Bi_2S_3 which is washed with hot water and weighed directly.

3. In the case of cadmium sodium sulphide gives a pure orange coloured precipitate of the sulphide which is washed with water and without any further treatment, weighed as CdS.

4. In the case of lead the solution is treated with alkali sulphide, the mixture is then acidified with acetic acid and the pure precipitate of PbS after washing with water weighed directly without heating.

5. In the case of indium treatment with ammonium sulphide gives a pure precipitate of In_2S_3 which after washing and heating can be weighed directly for the estimation of the metal. Equally good results are obtained if the mixture is acidified with acetic acid after treatment with ammonium sulphide.

6. The given procedures provide for a convenient, quick and accurate estimation of the metals.

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RÉSUMÉ

1. Il a été démontré que, dans des conditions déterminées, le bismuth, le cadmium, le plomb et l'indium, peuvent précipiter quantitativement comme sulfures purs, au moyen des sulfures alcalins. Le précipité obtenu peut être pesé directement en vue du dosage du métal.

2. Dans le cas du bismuth, le sulfure d'ammonium donne un précipité pur de Bi_2S_3 qui peut être lavé à l'eau bouillante et pesé directement.

3. Dans le cas du cadmium, le sulfure de sodium donne un précipité pur, orange, de sulfure, pouvant être lavé et pesé directement comme CdS.

4. Dans le cas du plomb, la solution est traitée avec un sulfure alcalin, le mélange est ensuite acidifié avec l'acide acétique et le précipité de PbS pur, après lavage à l'eau, peut être pesé directement sans chauffage.

5. Dans le cas de l'indium, le sulfure d'ammonium donne un précipité de In_2S_3 pur, qui, après lavage et chauffage peut être pesé directement pour le dosage du métal. On obtient également de bons résultats si l'on acidifie à l'acide acétique après traitement au sulfure d'ammonium.

6. Les procédés décrits permettent un dosage rapide et précis des métaux cités.

ZUSAMMENFASSUNG

1. Es wurde gezeigt, dass bei geeigneten Bedingungen Wismuth, Cadmium, Blei und Indium quantitativ mit Alkalisulfiden als reine Sulfide ausgefällt werden können und der Niederschlag direkt zur Bestimmung der Metalle gewogen werden kann.

2. Im Falle des Wismuths gibt Ammoniumsulfid einen reinen Niederschlag von Bi_2S_3, der mit heissem Wasser gewaschen und direkt gewogen wird.

3. Im Falle des Cadmiums gibt Natriumsulfid einen reinen orange gefärbten Niederschlag des Sulfids, der mit Wasser gewaschen wird und ohne weitere Behandlung als CdS gewogen wird.

4. Im Falle des Bleis wird die Lösung mit Alkalisulfid behandelt, die Mischung dann mit Essigsäure angesäuert und der reine Niederschlag von PbS nach dem Waschen mit Wasser ohne Erhitzen direkt gewogen.

5. Im Falle des Indiums gibt die Behandlung mit Ammoniumsulfid einen reinen Niederschlag von In_2S_3, der nach dem Waschen und Erhitzen zur Bestimmung des Metalls direkt gewogen werden kann. Gleich gute Ergebnisse erhält man, wenn die Mischung nach dem Behandeln mit Ammoniumsulfid mit Essigsäure angesäuert wird.

6. Die gegebenen Verfahren lassen eine bequeme, schnelle und genaue Bestimmung der Metalle zu.

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RAPID DETERMINATION OF THORIUM IN ORES
I. SEPARATION AS IODATE IN PRESENCE OF OXALIC ACID

by

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The most highly recommended and accepted procedure for the separation and estimation of thorium from other elements is the iodate method[1], the details of which are discussed in all the standard reference books. The method is most popular because of the excellence of the separations, the rapidity of the filtration of the crystalline precipitate and the ease of resolution. However, separations are not obtained from zirconium, titanium and bismuth, which constitute the only serious interferences[2]. Hence the iodate and oxalate separations must be carried out in conjunction, to separate thorium from almost all other cations.

According to KALL AND GORDON[3], thorium oxalate is not as quantitatively insoluble as one would infer from the literature and they think it desirable to avoid, whenever possible, the use of the oxalate procedure or to carry it out under stricter conditions as discussed in their paper.

In the improved procedure, suggested in this paper, the oxalate precipitation has been avoided altogether and thorium is finally precipitated as hydroxide after its major separation from all the other cations, by using potassium iodate in 40% nitric acid solution, simultaneously with oxalic acid, which serves as a strong complexing agent for zirconium, titanium and bismuth even in the presence of phosphate.

EXPERIMENTAL

It was found that (1) thorium-iodate is insoluble in 40% nitric acid and excess of potassium iodate, even in presence of 10% oxalic acid, (2) approximately 16 mg of titanium oxide, 46 mg of zirconium oxide and 112 mg of bismuth oxide are not precipitated as iodates in the presence of 25 ml of 10% oxalic acid in 40% nitric acid concentration and (3) in the presence of oxalic acid, the iodate precipitate settles down within ten minutes, when cooled in ice-cold water.

Estimation of thorium

A stock solution of thorium nitrate was prepared using A.R. thorium nitrate. Thorium content in this solution was determined by metanitrobenzoic acid and

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potassium iodate methods. From another aliquot, thorium was precipitated as iodate, in the presence of 10% oxalic acid, keeping 40% nitric acid concentration, the total volume depending on the oxalic acid required to complex interfering elements. The solution was cooled to room temperature for about ten minutes by placing the beaker in ice-cold water and was filtered through Whatman 540, 11 cm paper. The precipitate was washed with 1% potassium iodate in 10% nitric acid several times to free it from oxalic acid. The iodate precipitate was dissolved in hydrochloric acid with the help of sulphurous acid, precipitated as hydroxide, washed free from excess iodide, ignited and weighed as thorium oxide. Same filter paper was used throughout the estimation. Results are shown in Table I.

TABLE I

ESTIMATION OF THORIUM IN PRESENCE OF OXALIC ACID

Expt. No.	Thorium taken g	Oxide found g	
1	0.0520	0.0522	Iodate method
		0.0525	oxalic acid-iodate method
2	0.0990	0.0989	Iodate method
		0.0992	oxalic acid-iodate method

Estimation of thorium in presence of zirconium, titanium and bismuth

In another set of experiments, different quantities of zirconium, titanium and bismuth were added separately and together to thorium solution. Thorium was precipitated as iodate from the iodate-oxalic acid mixture. The precipitate washed

TABLE II

ESTIMATION OF THORIUM IN PRESENCE OF TITANIUM, ZIRCONIUM AND BISMUTH

Expt No.	Titanium taken mg	Zirconium taken mg	Bismuth taken mg	Thorium taken g	Oxide found g
1	5.25			0.0520	0.0521
2	21			0.0520	0.0520
3	20			0.0990	0.0993
4		5		0.0520	0.0519
5		40		0.0520	0.0521
6		40		0.0990	0.0989
7			5	0.0520	0.0525
8			20	0.0520	0.0518
9			20	0.0990	0.0992
10	10	4.1	5	0.0990	0.0989
11	5	20.5	10	0.0990	0.0991
12	10	10	10	0.0990	0.0990

first with 1% potassium iodate, 1% oxalic acid in 10% nitric acid and then with 1% potassium iodate in 10% nitric acid. In cases where amounts of interfering elements were large, a reprecipitation was carried out (Experiments 2, 3, 5, 6, 8 to 12 Table II). The precipitates were tested for titanium, zirconium and bismuth, which were found to be practically absent. Results are shown in Table II.

Estimation of thorium in presence of rare earth oxides, titanium, zirconium and bismuth

A stock solution containing thorium and rare earths as nitrates was prepared by separation from monazite sands. From an aliquot of the stock solution, thorium contents were determined by the new proposed method and the results compared with those obtained by the usual iodate method. A reprecipitation was carried out. Unlike the potassium iodate method, prior reduction of cerium (IV) is not necessary, as oxalic acid reduces ceric cerium (Experiment 1, Table III). In another set of experiments, varying amounts of titanium, zirconium and bismuth were added to the aliquots of the above solution and thorium precipitated in iodate-oxalic acid mixture. A reprecipitation was carried out in the presence of oxalic acid and the precipitate washed first four times with 10% nitric acid, 1% potassium iodate and 1% oxalic acid and subsequently with 1% potassium iodate in 10% nitric acid. The thorium was finally precipitated as hydroxide. The thoria was tested for and was found practically free from titanium, zirconium and bismuth. Results are shown in Table III.

TABLE III

ESTIMATION OF THORIUM IN PRESENCE OF CERIUM EARTHS, TITANIUM, ZIRCONIUM AND BISMUTH

Expt No.	Rare earths + Th oxide mg	TiO_2 taken mg	ZrO_2 taken mg	Bi_2O_3 taken mg	Thorium taken (Iodate method) g	Oxide found g
1	475				0.0612	0.0612
2	,,	6	4.1	6.6	0.0612	0.0609
3	,,	20			0.0612	0.0613
4	,,		16.4		0.0612	0.0611

Estimation of thorium in monazite sands

Finally the method was extended to the determination of thorium in monazite sands. 25 g monazite was fumed with 40 ml of sulphuric acid, until the sand had completely disintegrated and the resulting pasty mass was cooled to room temperature. Crushed ice was added directly to the mass. The suspension was filtered

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and washed with water. For analysis an aliquot of this solution corresponding to 1 g of original sand was diluted to 100 ml and thorium determined by this method (reprecipitating and washing with two wash liquids as given above) and the results compared against the values obtained by the usual iodate method. The precipitates were free from phosphate, sulphate, titanium, zirconium, bismuth and uranium. The results shown in Table IV experiments 1, 2, 3, agree well. The whole estimation by this method could be completed within 8 to 9 hours.

Estimation of thorium in monazite sands, with added bismuth, titanium and zirconium

The accuracy of this method was further tested by adding different quantities of titanium, zirconium and bismuth to the monazite solutions. The thorium oxide so obtained was found to be free from these added cations. The results are shown in Table IV, experiments 4 to 7.

TABLE IV

ESTIMATION OF THORIUM IN MONAZITE SAND ALONE AND AFTER ADDITION OF TITANIUM, ZIRCONIUM AND BISMUTH

Expt No.	Monazite taken 1 g	TiO_2 added mg	ZrO_2 added mg	Bi_2O_3 added mg	Thorium taken (Iodate method) g	Oxide found g
1	x				0.0625	0.0624
2	y				0.0945	0.0955
3	z				0.0858	0.0863
4	x	15			0.0625	0.0625
5	x		40		0.0625	0.0620
6	x			20	0.0625	0.0623
7	x	10	4.1	5	0.0625	0.0621

In the light of the above investigations a general procedure for direct estimation of thorium in ores may be laid down as follows:

1. Bring the sample in solution in the form of sulphates or nitrates (free sulphuric acid about 4%). Take 1 g sample for ores containing more than 5% thorium oxide. For samples containing about 0.1% thoria take 5 g.
2. Adjust the volume to 100 ml (for ores containing less than 1% thoria, adjust the volume preferably to 25 ml).
3. Add sufficient nitric acid so that after addition of oxalic acid in (4) the acidity of the final solution is 30% by volume.
4. Add sufficient amount of saturated solution of oxalic acid, the quantity depending on the amount of interfering ions in the solution.
5. Add 100 ml of 15% potassium iodate in 50% nitric acid for every 100 ml of the solution (final nitric acid 40% by volume).

6. Stir and allow the solution to cool to room temperature in ice cold water, for ten minutes.

7. Filter through Whatman No. 540, 11 cm paper, wash the precipitate four times with 1% potassium iodate and 1% oxalic acid in 10% nitric acid and then again four times with 1% potassium iodate in 10% nitric acid.

8. Transfer the precipitate back to the beaker by about 30-40 ml distilled water and reprecipitate, cool and wash as in (5) to (7) above.

9. Transfer the precipitate back to the beaker and dissolve in hydrochloric acid with the help of sulphurous acid. Wash the filter paper on the funnel with hot 1:3 hydrochloric acid, to which a few ml of sulphurous acid are added and then many times with water. Collect all washings in the beaker.

10. Boil the solution for a few minutes and precipitate thorium as hydroxide by adding 10 percent excess ammonia, add filter paper pulp and keep the solution on water bath for ten minutes. Filter through the same filter paper, which is washed previously with ammonia-ammonium nitrate wash liquid.

11. Wash the precipitate six times with ammonia-ammonium nitrate wash liquid, ignite to 1100° C and weigh as thorium oxide.

Further work on the estimation of trace amounts of thorium in ores is in progress.

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SUMMARY

It has been shown that thorium could be precipitated quantitatively in 40% nitric acid solution as iodate, in presence of oxalic acid which complexes all those elements that interfere seriously in the usual iodate procedure. Thorium is thus freed from all the cations in a single operation from solutions containing sulphate and phosphate radicals. The method is very quick and thorium oxide in a sample of monazite could be estimated with precision in 8-9 hours.

RÉSUMÉ

Il est possible de précipiter quantitativement le thorium, en solution dans l'acide nitrique à 40%, comme iodate; on effectue cette précipitation en présence d'acide oxalique, pour complexer tous les éléments qui gênent le dosage. Le thorium peut ainsi être séparé de tous les cations en une seule opération, en solution renfermant des anions sulfuriques et phosphoriques. La méthode est très rapide, l'oxyde de thorium d'un échantillon de monazite peut être dosé avec précision en 8-9 heures.

ZUSAMMENFASSUNG

Es wurde gezeigt, dass Thorium in 40%iger Salpetersäure quantitativ als Jodat gefällt werden kann; die Fällung wird in Gegenwart von Oxalsäure vorgenommen, welche alle störenden Elemente als Komplexe bindet. Das Thorium kann auf diese

References p. 67.

Weise in einer einzigen Operation in Lösungen welche Sulphat- und Phosphatreste enthalten quantitativ von allen Kationen getrennt werden. Die Methode ist sehr rasch: in einer Probe von Monazit konnte das Thoriumoxyd innerhalb von 8-9 Stunden genau bestimmt werden.

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QUALITATIVE AND QUANTITATIVE ANALYSIS OF MIXTURES OF SULFONAMIDES. IX

by

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The determination of the total amount of sodium

In the previous papers we discussed some methods for the quantitative analysis of mixtures of therapeutically important sulfonamides without separation of the individual compounds (the principles have been outlined[118]). To end with, we shall now briefly describe the determination of the amount of soluble sodium salts in the mixture by way of the sodium content.

0.5-1 g of the mixture is placed in a porcelain crucible and moistened with a few drops of concentrated sulfuric acid. The crucible is then *very carefully* and *slowly* heated to drive off all sulfuric acid (1-2 hours). Next, the residue is thoroughly heated to destroy the organic matter; finally, pyrosulfate is transformed into sulfate by heating for a short time on a blowing-torch or Meker-burner. Melting alkali-salts, however, often envelop small coal-particles which are in consequence not burnt. If therefore the residue (consisting of pure sodium sulfate) is not of a pure white colour, another few drops of concentrated sulfuric acid together with two drops of concentrated nitric acid are added and the residue heated as before. The substance is weighed as pure sodium sulfate.

The various pure sodium sulfonamides gave always very good results, values found varying from 98.6 to 101.7% of the theoretical sodium contents.

The application to mixtures has also proved to give satisfactory results. A few examples are mentioned in Table XXV.

TABLE XXV

Compound	Quantity in g	Found %
Na-sulfadiazine	0.6319	99.4
Na-sulfamerazine	0.7053	99.7
Na-sulfamezathine	0.6947	
Na-sulfathiazole	0.6687	100.3
Na-sulfamerazine	0.6139	99.9
Na-sulfamezathine	0.6904	
Na-sulfapyridine	0.9085	98.8
Na-irgamid	0.8479	99.5

References p. 73.

Quantitative analysis of a mixture after previous separation of the components

It must, first of all, be possible to separate the individual sulfonamides quantitatively from each other.

This implies that little use can be made of differences in solubility, as may be seen in the first paper of this investigation where a list of solubilities is given[117]. Only in exceptional cases are these differences so large as to make a quantitative separation on this basis possible. The same may be said of the use of solvents after preparation of certain derivatives of the constituting sulfonamides (glucoside sulfonates[109], N-acetyl-products[110]).

Thus, better possibilities are to be expected from chromatographic methods of separation; lately, the use of ion-exchange columns has also been reported for this purpose[111].

In our investigation we used the chromatography on filter paper for the separation of the compounds, and tried to determine their quantities without extraction from the paper. The determination after extraction from the paper will only shortly be discussed below.

I. FISHER *et al.*[112] have demonstrated for a number of amino acids and sugars that a direct proportionality exists between the area of the spot on a chromatogram and the logarithm of the amount of compound present. BRIMLEY[113] has proved this for the general case. Though the method using this principle is not as accurate as the one described previously[118], it is attractive because of its simplicity.

In our experiments, sheets of Whatman No. 2 filter paper of 10 × 10″ were used. Known quantities of the compounds to be investigated were placed on the paper using 0.1% solution in acetone (method: *cf.*[114]). The elution was carried out with the solvents butanol/pyridine and butanol/ammonia/water[114]. After elution the spots were sprayed with the dilute *p*-dimethylaminobenzaldehyde reagent[114]. Their areas were then measured by placing a sheet of transparent graph-paper on the chromatogram, tracing the boundaries of the spots and counting their areas in square millimetres.

Results of various experiments with three sulfonamides are represented in Table XXVI and Figs. 27 and 28. They clearly show that a direct proportionality between the area of the spot and the logarithm of the concentration also exists here. Deviations from linearity are sometimes rather large, amounting to 15% in a few cases. This makes it advisable to run duplicate or triplicate analyses of unknown mixtures, which, however, can very easily be done on the same sheet of filter paper.

The increase in *colour-intensity* and length of a spot with increasing quantity of compound has been used by BRENNER *et al.*[115] for semiquantitative determinations. The accuracy of their method is not large, however, and certainly inferior to the one described by us. We therefore did not consider the colour-intensity of the spots, and restricted our experiments to concentrations where the linearity mentioned holds. The upper limit in this respect proved to be about 8 γ ($8 \cdot 10^{-6}$ g) of sulfonamide per spot.

The inclination of the straight lines (Figs. 27 and 28) of course will depend on many factors: sort of paper, composition and pH of developer, temperature, etc. It is thus necessary to compare the areas measured in the sample with a gauge-chromatogram prepared under exactly the same conditions as the sample-chromatogram. For that purpose eight known quantities of the compounds present are developed together with the sample in the way described above.

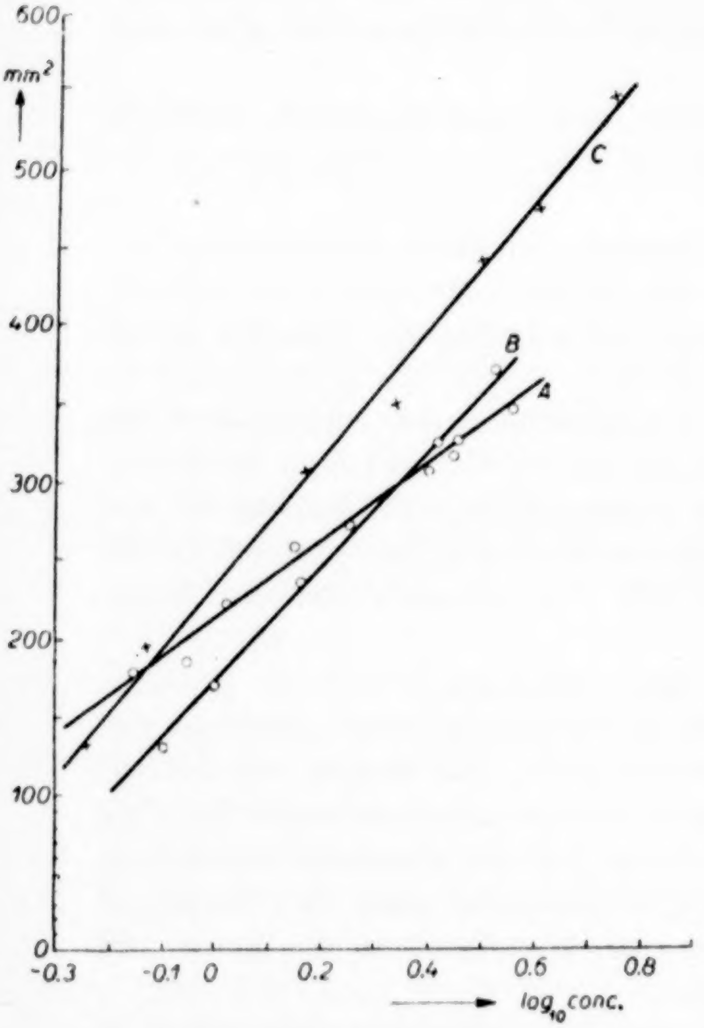

Fig. 27. Solvent: butanol/pyridine
A Sulfadiazine
B Sulfamerazine
C Sulfamezathine

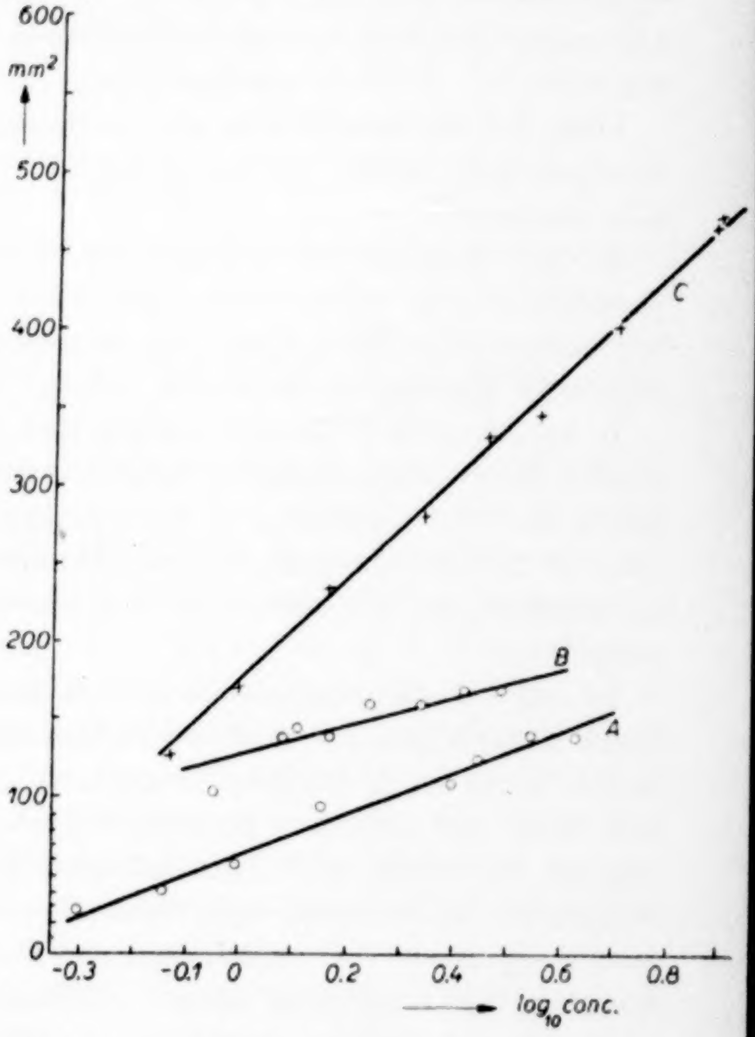

Fig. 28. Solvent: butanol/ammonia/water
A Sulfadiazine
B Sulfamerazine
C Sulfamezathine

In our experiments with different compounds the proper R_F-values proved to be practically independent of the concentration. The maximum deviation found was 5% for sulfamezathine, developed with butanol/pyridine: $R_F = 0.63$ at 0.57 γ per spot and 0.66 at 5.63 γ per spot.

Determination of the area of various spots in one chromatogram is, of course,

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only possible with reasonable accuracy if the latter are well separated and do not show the effect of "tailing". With mixtures of sulfadiazine, sulfamerazine and sulfamezathine "tailing" appeared when the amount of compound surpassed 2-2.5 γ per spot. With "tailing" deviations from linearity always occurred of ± 10%.

TABLE XXVI

Compound	Butanol/ammonia/water				Butanol/pyridine			
	γ	$\log_{10}\gamma$	mm^2	Deviation (%) from linearity	γ	$\log_{10}\gamma$	mm^2	Deviation (%) from linearity
Sulfa-diazine	0.502	—0.29930	27	—4	0.717	—0.14448	176	0
	0.717	—0.14448	42	+1.6	1.075	0.03141	225	—1
	0.931	—0.03105	58	—1.4	1.434	0.15655	258	—6.5
	1.434	0.15655	95	—18	1.793	0.25358	278	+1.7
	2.505	0.39881	112	+11	2.506	0.39898	310	+5.5
	2.863	0.45682	124	0	2.863	0.45682	326	0
	3.581	0.55400	138	0	3.581	0.55400	350	0
	4.300	0.63347	140	+10				
Sulfa-merazine	0.879	—0.05601	105	+67	0.782	—0.10679	133	+2
	1.218	0.08565	139	—7.6	0.879	—0.05601	187	—17
	1.271	0.10415	146	—12	0.977	—0.01011	172	0
	1.468	0.16673	140	+6.5	1.468	0.16673	234	0
	1.761	0.24576	158	—14	2.640	0.42160	325	0
	2.260	0.35411	160	0	2.836	0.45271	316	+15
	2.736	0.43712	168	0	3.322	0.52140	375	—4.3
	3.124	0.49471	170	+3.3				
Sulfa-mezathine	0.740	—0.13077	128	+4.5	0.574	—0.24109	133	0
	1.010	0.00432	173	+3.4	0.740	—0.13077	195	—8
	1.479	0.16997	234	—2	1.479	0.16997	305	—2
	2.219	0.34616	280	+4.2	2.219	0.34616	350	+14
	2.960	0.47129	330	—2.3	3.250	0.51295	440	0
	3.700	0.56820	345	+10	4.142	0.61721	475	+4
	7.840	0.89432	462	+1.3	5.632	0.75066	544	—3.3
	5.036	0.70209	398	0				
	7.951	0.90042	467	—3				

Good separations of the compounds can only be achieved if a proper solvent is chosen for the elution. This subject has been amply discussed in our fifth paper. The directions given there can be used here without any alteration, except for the use of the narrow strips of filter paper, however. Their use is impossible here, one of the conditions of our method being the unimpeded diffusion of the compounds[113].

In the examples given above we mentioned in full detail our results with sulfamerazine, sulfamezathine and sulfadiazine. Without further specifying the areas we give in Table XXVII a survey of other separations. Gauge-curves were determined by running together with each mixture known quantities of the compounds present. Of each compound eight different quantities were always taken (ranging from about 0.4 to 2.8 γ), using an acetone-solution and a calibrated micro-pipet. The chromatograms of the gauge-quantities and the samples were always developed at the same time, with the same solvent and on the same paper. The solvent was butanol/ammonia/water in the first three separations and butanol/pyridine in the latter two.

From the figures obtained the conclusion must be drawn that the method yields fairly good results, and therefore may be called attractive when simplicity of operation is preferred above high exactness of results.

TABLE XXVII

Compounds	Taken γ	Found γ			Mean γ	Mean % from theory	Max. deviat. from mean (%)
Irgafen	1.50	1.44	1.40	1.45	1.43	95.3	—2.1
Sulfanilamide	0.95	1.03	0.89	1.00	0.97	102.1	—8.2
Sulfamerazine	1.85	1.87	1.80	1.82	1.83	98.8	+2.1
Irgafen	1.00	1.10	1.09	1.11	1.10	110.0	±0.9
Sulfaguanidine	0.80	0.76	0.79	0.85	0.80	100.0	+5.9
Sulfamethylthiazole	1.75	1.77	1.78	1.76	1.77	101.0	±0.6
Sulfathiazole	1.25	1.29	1.34	1.31	1.31	95.4	+2.3
Sulfamezathine	1.75	1.81	1.81	1.78	1.80	102.9	—1.1
Elkosin	1.00	0.98	0.94	0.96	0.96	96.0	±2.1
Sulfanilamide	1.50	1.52	1.49	1.52	1.51	100.5	—1.3
Sulfadiazine	1.50	1.47	1.46	1.53	1.49	99.3	+2.7

II. In the chromatographic separation of sulfonamides on paper microgram quantities are always used. One is thus forced to use microtechniques in the removal of the compounds from the paper and their subsequent determination. Spectrophotometric methods have thus far in a few instances been mentioned for this purpose. THOMAS *et al.*[65] determined in this way the composition of two mixtures (*viz.* sulfadiazine/sulfamerazine/sulfamezathine and sulfadiazine/sulfamerazine/sulfathiazole).

WAGNER[116] in an extensive investigation analyzed several mixtures of sulfonamides after separation, extraction and colouring with sodium nitrite and thymol. Since the coloured solutions are made up to 12.5 ml, their colour-intensity is relatively far less than the one of the spots described by us. The quantities present in WAGNER's chromatograms had therefore to be ten to fifty times as large as in ours. Moreover, in extracting the compounds from the paper an unavoidable irregular extraction loss always appears, which from a few percents may amount up to ten per cent or even more[116]. This makes it questionable whether these time-consuming spectrophotometric methods are really *far more* accurate than the one described by us.

At the time of this investigation we had no spectrophotometer at our disposal and therefore could not study mixtures of sulfonamides in this respect.

ACKNOWLEDGEMENT

We are indebted to Miss E. G. SNIJDOODT and to Mr. A. DE JAGER for their valuable technical assistance. The following companies kindly placed pure sulfonamides at our disposal: N.V. Amsterdamsche Chininefabriek, N.V. Ciba, N.V. Soc. voor Chem. Industrie "Katwijk", I.C.I. (Holland) N.V., Dagra N.V. and "Propharma" (Haarlem).

SUMMARY

In our final paper in this series we first discuss a determination of the sodium content.

A rapid quantitative estimation of a mixture of sulfonamides is possible after separation of the components by means of paper chromatography without their removal from the paper. The linear relationship between the area of a spot on the chromatogram and the logarithm of the amount of compound present forms the basis of this method.

RÉSUMÉ

Dans son dernier mémoire de cette série, l'auteur étudie d'abord le dosage du sodium, puis un dosage quantitatif et rapide d'un mélange de sulfamidés, par chromatographie sur papier, sans extraction.

Le procédé proposé est basé sur le fait que la surface d'une tache est en relation linéaire avec le logarithme de la concentration de la substance présente.

ZUSAMMENFASSUNG

In unserer letzten Veröffentlichung dieser Reiche besprechen wir zuerst die Bestimmung des Natriumgehalts.

Eine schnelle quantitative Bestimmung einer Mischung von Sulfonamiden ist möglich nach Trennung der Komponenten mit Hilfe von Papierchromatographie ohne ihre Entfernung vom Papier. Die lineare Beziehung zwischen der Fläche eines Flecks auf dem Chromatogram und der Logarithmus der Menge der diesbezügliche Substanz bildet die Grundlage dieser Methode.

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GRAPHICAL ANALYSIS OF STYRENATED LINSEED OILS

by

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INTRODUCTION

In a former publication[1] a new method for the preparation of homogeneous styrenated linseed oils was described according to which styrene vapours were brought into contact with the oil at temperatures of approx. 280° C.

Calculation of the amount of styrene in the products is possible by means of the saponification value. Determination of this value, however, is rather laborious and inaccurate because of difficulties in the saponification process and the back-titration of the excess of lye.

In the course of our investigations a graphical method was developed, based on determinations of n_D^{20} and d_4^{20}, allowing an accurate and reliable estimation of the percentage of styrene in linseed oils, styrenated according to the method mentioned above.

EXPERIMENTAL

Styrenated linseed oils were prepared by reaction of styrene vapours with linseed oil in a batch apparatus described elsewhere[1]. By varying the reaction conditions (reaction time, temperature, amount of nitrogen used as a carrier gas for the styrene vapours), a number of oil samples of widely different styrene content could be assembled.

The styrene content was determined directly by weighing the amount of linseed oil before and after each styrenation process. However, a small correction had to be made in connection with losses in weight of the oil due to evaporation of volatile components (*e.g.*, free fatty acids) during the styrenation process, especially at higher temperatures. These corrections could be established for each distinct case by blank experiments, in which vapours of ethyl benzene instead of styrene were brought into contact with linseed oil and partly styrenated linseed oils under corresponding reaction conditions.

A second possibility to calculate the amount of styrene, taken up by the linseed oil, gives the saponification value. This value was determined by boiling 1-2 g of the styrenated oil for 1½ hrs with 25 ml 0.5N alcoholic potassium hydroxide solution and 25 ml toluene, and neutralizing the excess of KOH with 0.5N standard

HCl solution. The titer of the alcoholic KOH follows from a blank. By comparison of the saponification values of linseed oil before and after styrenation the amount of styrene in the product can be easily calculated.

A graphical determination of the amount of styrene is possible by means of refractive index (d^{20}_D) and density (n^{20}_4). This is shown in Fig. 3. The graph is based on the fact that thermal polymerization of linseed oil and styrene can be represented in a good approximation by two parallel straight lines in the n — d graph.

The data of thermal polymerized linseed oil (*Fig.* 1) are partly adopted from the literature[2], partly from new experiments at different temperatures (Table I).

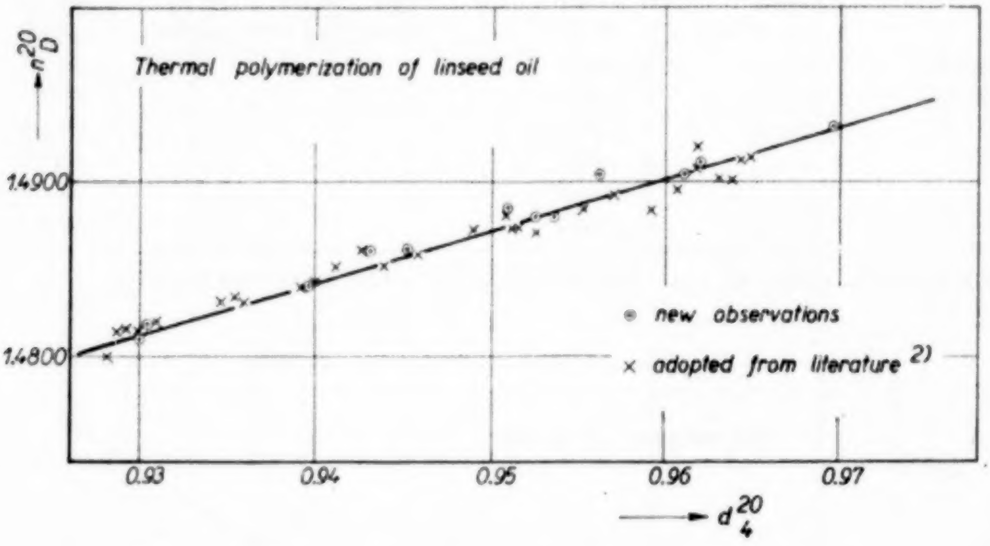

Fig. 1. Thermal polymerization of linseed oil

TABLE I

THERMAL POLYMERIZATION OF LINSEED OIL IN A NITROGEN STREAM*

	Constants of Starting Material	Reaction conditions temp. °C	reaction time (hrs)	Constants of polymerized oils n^{20}_D	d^{20}_4
A 1	$n^{20}_D = 1.4819$	290	1.5	1.4861	0.9431
2		290	3	1.4885	0.9510
3	$d^{20}_4 = 0.9305$	290	4.5	1.4904	0.9562
4		290	6	1.4920	0.9618
B 5		280	4	1.4862	0.9452
6		290	4	1.4880	0.9526
7	$n^{20}_D = 1.4810$	300	4	1.4910	0.9620
8	$d^{20}_4 = 0.9300$	310	4	1.4932	0.9697
C 9		280	4	1.4840	0.9396
10		300	4	1.4880	0.9537
11		340	1/4	1.4904	0.9612

* The experiments 1—4 were carried out by Mr. A. A. VAN DEN BERGH.

The data of styrene polymers were collected by polymerization of pure styrene under different conditions (Table II and Fig. 2).

TABLE II

PHYSICAL CONSTANTS OF STYRENE POLYMERIZED UNDER DIFFERENT CONDITIONS

Product	n_D^{20}	d_4^{20}	Product	n_D^{20}	d_4^{20}
Styrene	1.5453	0.9059	Styrene	1.5470	0.9064
Polymerized thermally 100—120° C	1.5570	0.9400	Styrene, polymerized at room temperature with 0.05% benzoyl peroxide*	1.5480	0.9098
	1.5610	0.9498		1.5500	0.9157
	1.5498	0.9193		1.5529	0.9247
	1.5516	0.9239		1.5551	0.9316
Polymerized at room temperature, u.v. irradiation	1.5534	0.9297		1.5578	0.9401
	1.5570	0.9400		1.5606	0.9483
	1.5574	0.9409		1.5630	0.9580
	1.5602	0.9482		1.5658	0.9654
	1.5610	0.9498		1.5672	0.9696
	1.5720	0.9850		1.5699	0.9819

* Experiments, carried out by Mr A. A. VAN DEN BERGH.

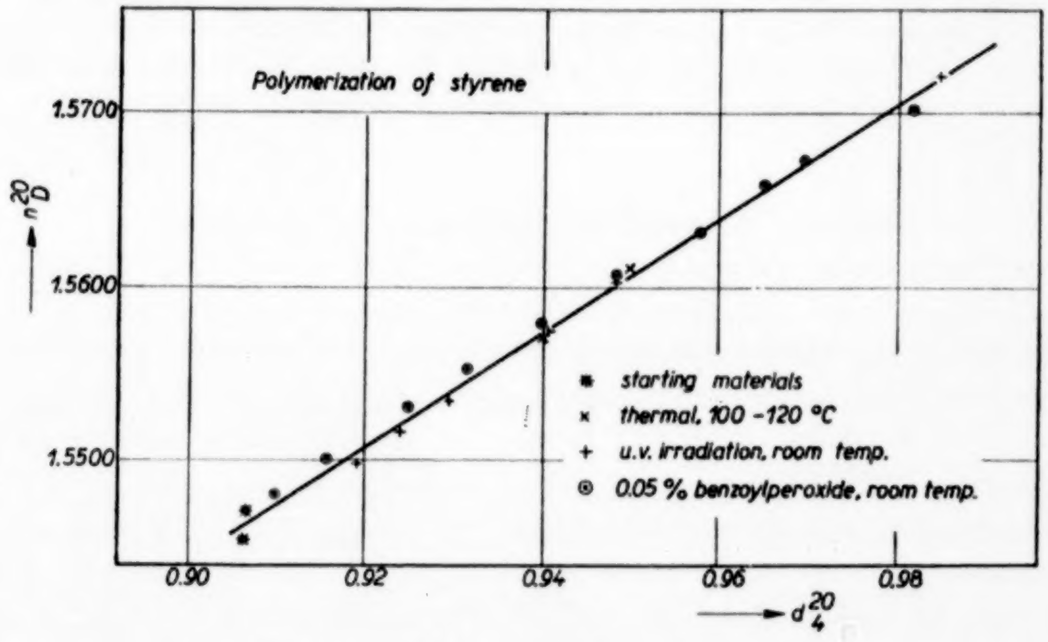

Fig. 2. Polymerization of styrene

In Fig. 3 curves are drawn between the polymerization curves of styrene and linseed oil indicating the percentage of styrene in styrenated linseed oils.

In Table III the results of the graphical analyses are compared with the styrene contents determined directly from the difference in weight before and after styrenation, and from the saponification values.

It can be concluded that the results of the graphical analysis are in good agree-

References p. 78.

ment with those of the other methods. Graphical analysis therefore allows a quick and accurate determination of the styrene content of styrenated linseed oils.

The data of Fig. 3 only concern styrenated oils, which, as a consequence of their special method of preparation, contain no polystyrene[1]. The applicability of the graphical method to other styrenated oils has not yet been proved, except for one commercial product (see Table III).

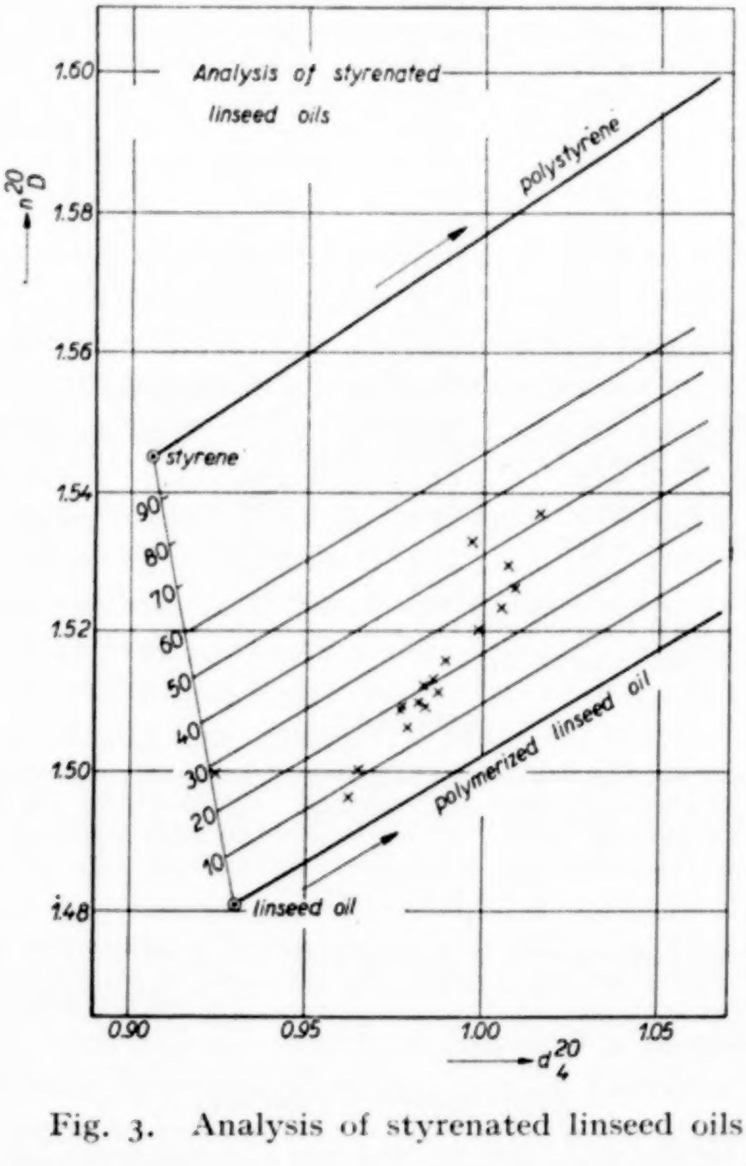

Fig. 3. Analysis of styrenated linseed oils

Graphical analysis of styrenated linseed oils is also possible by using the specific refraction $\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$ combined with density or refractive index. This results in similar graphs as discussed above for the application of density and refractive index.

References p. 78.

TABLE III

ANALYSIS OF STYRENATED LINSEED OILS

No.	Reaction Conditions		Properties of Styrenated Oils			Styrene content		
	Reaction time hrs.	Temp. °C	n^{20}_D	d^{20}_4	Saponification value	from weight increase during styrenation	from saponif. value	from n^{20}_D and d^{20}_4
0	Non styrenated linseed oil		1.4810	0.9300	190			
1	1	300	1.4965	0.9609	—	7	—	8
2	2	280	1.5001	0.9647	171	10	10	11
3	2	300	1.5062	0.9785	—	14	—	14
4	4	280	1.5092	0.9831	160	17	16	16
5	3	300	1.5112	0.9869	—	18	—	17
6	3	280	1.5099	0.9812	158	17	17	18
7	4	280	1.5090	0.9764	158	19	17	19
8	4	270	1.5093	0.9767	152	18	20	19
9	4	280	1.5123	0.9830	152	21	20	20
10	4	280	1.5132	0.9853	151	21	21	21
11	4	280	1.5126	0.9828	151	21	21	21
12	4	280	1.5158	0.9890	145	22	24	23
13	4	290	1.5202	0.9982	141	25	26	25
14	4	300	1.5235	1.0050	143	26	25	27
15*	—	—	1.4995	0.9241	—	29	—	28
16	4	310	1.5262	1.0085	138	24	27	29
17	7	280	1.5294	1.0069	123	34	35	34
18	10	280	1.5370	1,0155	111	42	42	42
19**	—	—	1.5330	0.9960	106	—	44	44

* mixture of styrene and linseed oil.
** commercial styrenated linseed oil.

SUMMARY

A graphical method for the analysis of styrenated linseed oils prepared by reaction of linseed oil with gaseous styrene is described. The method allows determination of the percentage of styrene from refractive index and density.

RÉSUMÉ

Une méthode graphique a été développée pour l'analyse des huiles de lin styrénisées, préparées par réaction d'huiles de lin avec le styrène à l'état gazeux.

La méthode permet la détermination du pourcentage en styrène, lorsqu'on connait l'indice de réfraction et la densité.

ZUSAMMENFASSUNG

Eine graphische Methode für die Analyse von styrenisierten Leinölen, dargestellt durch die Reaktion mit gasförmigem Styren, wurde entwickelt.

Die Methode erlaubt uns den Prozentsatz vom Styren zu bestimmen, wenn man den Brechungsindex und die Dichte kennt.

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ÉTUDE SUR LE DOSAGE COLORIMÉTRIQUE DU CUIVRE AU DIÉTHYLDITHIOCARBAMATE (EN MILIEU SODIQUE)

par

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1. En vue du dosage colorimétrique du cuivre par le diéthyldithiocarbamate de sodium (DDC), JEWSBURY[1] rappelle que le nickel donne, au même titre que le cuivre, une coloration brune avec ce réactif, dans le milieu classique ammoniacal citrique. Il est fait mention dans le travail cité des inconvénients liés à la séparation préalable du nickel par la diméthylglyoxime, initialement indiquée par les auteurs de langue anglaise.

2. L'auteur rappelle également la technique de STEELE ET RUSSELL[2] selon laquelle l'augmentation de l'alcalinité ammoniacale tend, tout en supprimant la séparation préalable du nickel par la diméthylglyoxime, à éliminer la coloration propre de ce métal avec le réactif DDC; toutefois il note que, dans ce milieu le nickel entraîne encore une légère coloration, et que cette méthode ne saurait convenir pour le dosage des petites quantités de cuivre.

3. S'agissant du dosage du cuivre dans la soude technique, JEWSBURY étudie un mode opératoire, selon lequel le nickel est complexé par l'acide éthylènetétra-acétique (trilon B), afin d'éliminer l'influence perturbatrice de ce dernier élément.

4. J'ai montré antérieurement, qu'en milieu sodique, l'influence du nickel est entièrement éliminée, alors qu'en milieu alcalinisé par l'ammoniaque cette perturbation subsiste bien[3].

La technique, tout d'abord donnée à propos du dosage du cuivre dans les aciers[4] a été étudiée de nouveau[3] et appliquée à l'analyse des alliages légers[5].

5. CHILTON[6] indique les courbes d'absorption des diéthyldithiocarbamates de cuivre, de nickel et de cobalt en milieu pyrophosphorique-ammoniacal; celles-ci permettent de remarquer que vers 450 mμ, l'absorption du complexe du nickel est en fait bien inférieure à celle du complexe cuivrique.

6. Prenant en exemple le dosage du cuivre dans le cas des alliages légers, déjà étudié par le moyen du milieu sodique-tartrique[5], je me suis proposé d'envisager si l'introduction de trilon apporterait une amélioration en vue de l'élimination de l'influence du nickel.

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7. Chacun des essais porte sur 0.02 g d'aluminium (99.8% environ) que l'on attaque par 5 ml du mélange acide (acide chlorhydrique 1.18: un volume; acide nitrique 1.33: un volume; eau: deux volumes).

Des volumes variables de solution de cuivre (0.0392 g/l $SO_4Cu.5H_2O$; 1 ml = 10 γ Cu, soit 0.05% Cu pour la prise d'essai de 0.02 g d'aluminium), et de solution de nickel (1.45 g/l $SO_4Ni.7H_2O$; 1 ml = 0.3 mg Ni soit 1.5% Ni pour la prise d'essai de 0.02 g d'aluminium) pourront être ajoutés après l'attaque.

Ajouter successivement: 5 ml de solution d'acide tartrique (au demi); de l'hydroxyde de sodium (400 g/l) pour neutraliser et 15 ml en excès; le trilon B (solution $M/50$, soit 5.842 g/l de l'acide, dissous à la faveur d'une quantité suffisante d'hydroxyde de sodium); le sulfate de magnésium (10.14 g/l $SO_4Mg.7H_2O$ dont 1 ml = 1 mg Mg); 5 ml de solution aqueuse de DDC (1 g/l); l'on extrait enfin au moyen de 50 ml au total de tétrachlorure de carbone*.

8. Une gamme de référence est d'abord faite, et comportant 0 à 100 γ Cu, sans nickel, ni trilon, ni magnésium. On sait au reste (5) que le nickel serait sans influence dans un tel milieu.

9. JEWSBURY montre que le *magnésium* introduit afin d'éliminer l'excès de trilon, servant à complexer le nickel et qui complexerait le cuivre et conduirait ainsi à des résultats erronés par défaut, ne doit pas être en large excès vis-à-vis du trilon. L'auteur indique: 3 mg Mg pour 10 ml d'une solution de trilon deux fois moins concentrée que celle dont il est fait usage présentement.

Or, il serait nécessaire d'augmenter la quantité de trilon, si celui-ci complexait de l'aluminium, afin de conserver son pouvoir complexant vis-à-vis du nickel. Il a été vérifié que cet écueil n'est pas à redouter: dans trois séries d'essais, en présence de 0.2 g Al et de 100 γ Cu, on a ajouté respectivement 75 ml — 50 ml et 20 ml de solution de trilon $M/50$, et des quantités variables de solutions de sulfate de magnésium, à 76.05 g/l dans la première, à 50.7 g/l dans la seconde, à 10.14 g/l dans la troisième série.

Toutes ces séries donnent des résultants constants pour le dosage du cuivre: le trilon est donc sans action sur l'aluminium.

10. Les séries suivantes ont pour but d'étudier l'influence du trilon sur le dosage du cuivre dans le milieu tartrique-sodique.

Aux attaques de 0.02 g Al, on ajouté 100 γ Cu, 5 ml de la solution tartrique, la soude, 10 ml de trilon ($M/50$), des *doses variables de magnésium* (0 à 10 mg Mg), le réactif DDC et l'on extrait au tétrachlorure.

Les lectures photométriques indiquent un résultat constant, identique d'ailleurs à celui des séries précédentes.

11. Dans deux séries à *cuivre variable*, on met en œuvre, après l'attaque de l'aluminium, des doses échelonnées de 0 à 100 γ Cu, puis on ajoute l'acide tartrique, l'hydroxyde de sodium, 10 ml de trilon ($M/50$); 10 ml de solution de sulfate de

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* Mesures photométriques: cuves de 2 cm, $\lambda = 460$ mμ, spectrophotomètre JEAN et CONSTANT.

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magnésium (1 ml = 1 mg Mg) dans l'une, et 2.5 ml dans l'autre série; le réactif DDC et le tétrachlorure.

Les résultats de l'une et l'autre série sont identiques à ceux qu'a donnés la série exempte de trilon (§ 8).

Les essais, relatés dans ce paragraphe et dans le précédent, montrent que le trilon lui-même n'a dans le milieu étudié aucune influence sur la réaction du cuivre au DDC.

12. Si, en présence de doses constantes de cuivre (100 γ), on ajoute des *doses variables de nickel* (jusqu'à 3 mg Ni) en présence de 10 ml de trilon ($M/50$) et de 2.5 ml de solution de sulfate de magnésium (10.14 g/l) dans une série, et de 10 ml de cette solution dans l'autre série, on observe que les résultats sont tous constants.

13. Inversement, si à une quantité fixe (3 mg) de nickel, on ajoute des doses *variables la cuivre* (0 à 100 γ), on observe par les mêmes modes opératoires, que les résultats sont identiques à ceux que donne la série de référence (§ 8).

14. Enfin, si à des *doses constantes de cuivre* (100 γ) *et de nickel* (3 mg) on ajoute 10 ml de trilon ($M/50$) et des *quantités variables* (0 à 10 ml) *de solution de sulfate de magnésium* (0 à 10 mg Mg), les chiffres lus sont tous constants.

15. Des essais relatés aux paragraphes 12 - 13 et 14, il ressort qu'en milieu sodique, le trilon est sans effet tant sur le cuivre que le nickel, et que la coloration parasite de celui-ci n'apparaît pas.

Le milieu sodique-tartrique suffit donc, à lui seul, pour inhiber la coloration due au nickel.

RÉSUMÉ

Dans le dosage colorimétrique du cuivre par le diéthyldithiocarbamate de sodium, le milieu sodique-tartrique empêche le développement de la coloration parasite due à la présence éventuelle du nickel. L'introduction de trilon ne procure aucun avantage supplémentaire.

SUMMARY

In the colorimetric determination of copper by sodium diethyldithiocarbamate, the alkaline-tartaric medium prevents the development of the parasitic coloration due to the presence of nickel. The introduction of trilon has no effect in alkaline medium.

ZUSAMMENFASSUNG

Bei der kolorimetrischen Bestimmung des Kupfers mit Natriumdiäthyldithiocarbamat verhindert das alkalisch-weinsaure Medium die Entwicklung der dem Nickel zuzuschreibenden Nebenfärbung. Die Einführung von Trilon bringt keine zusätzlichen Vorteile mit sich.

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SUR LE DOSAGE COLORIMÉTRIQUE DE L'ANTIMOINE AU VIOLET DE MÉTHYLE

par

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La réaction au violet de méthyle, qui a fait l'objet de publications de notre part[1], est étudiée de nouveau par GOTO ET KAKITA[2], selon un mode opératoire assez semblable à celui qui sert au dosage de l'antimoine à la rhodamine (LUKE[3], WHITE ET ROSE[4] en particulier).

Les auteurs japonais proposent de remplacer le benzène initialement employé [1] par l'acétate d'amyle.

En milieu benzénique le complexe coloré est bleu-violet et vire au violet avec le temps, d'où nécessité de conserver les essais à l'obscurité et de faire les mesures colorimétriques sans tarder. L'acétate d'amyle donnerait au contraire des milieux violets stables.

L'on a opéré selon la technique des auteurs: A 5 ml d'acide chlorhydrique 6*N*, contenant l'antimoine à doser, ajouter 0.3 ml de sulfate cérique (2%), 5 ml de solution de sulfate d'hydrazine (1%) et 1 ml de solution de violet de méthyle (0.2%); puis 10 ml de solution de citrate de sodium (300 g/l). Si la liqueur n'est pas bleu-vert à vert, ajouter de l'acide chlorhydrique 6*N* si elle est violette ou bleue, ou du citrate si elle est jaune, de manière à la ramener à la teinte voulue (bleu-vert à vert). Compléter à 25 ml environ avec de l'eau.

Extraire par 5 ml d'acétate d'amyle.

Après la première extraction, dans un essai *exempt d'antimoine*, les 5 ml d'acétate d'amyle sont légèrement colorés en violet. Si l'on opère 3 extractions ultérieures au moyen de 5 ml du solvant, on constate que ces liquides extraits sont également colorés, toutefois la coloration allant en diminuant dans les dernières opérations.

Dans un essai portant sur 10 γ d'antimoine, la coloration extraite par les 5 premiers millilitres de solvant se montre très semblable en intensité à celle de l'essai zéro, et, de même, les extractions ultérieures présentent des colorations se situant comme celles faites successivement avec l'essai zéro.

Pour une même quantité d'antimoine, augmenter la dose d'acétate d'amyle ajouté dans la première affusion, conduit à obtenir un liquide d'extraction présentant une coloration plus intense, que si l'on employait seulement les 5 ml prévus par les auteurs japonais.

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L'acétate d'amyle provoque donc une extraction du violet de méthyle lui-même, et non spécifiquement du complexe antimonique.

La gamme d'essais suivantes a été faite, au moyen de l'extraction benzénique, mais selon la technique de GOTO ET KAKITA. A des volumes variables d'une liqueur d'antimoine (1 ml = 10 γ Sb) dans l'acide chlorhydrique 6*N*, ajouter des quantités variables d'acide chlorhydrique 6*N* telles que le volume total soit 5 ml; puis 1.2 ml de solution de sulfate cérique (5 g/l d'eau sulfurique à 30 ml SO_4H_2, d = 1.83 par litre), 5 ml de solution de sulfate d'hydrazine (10 g/l), 1 ml de solution de violet de méthyle (2 g/l) et 10 ml de solution de citrate de sodium à 300 g/l. On procède à l'extraction au moyen de benzène et l'on complète à 25 ml. Mesurer photométriquement (γ = 615 mμ).

γ Sb	mesures photométriques
50	65 → 100
40	80
30	64
25	50
20	21
10	4
0	0

RÉSUMÉ

La technique d'oxydation au sulfate cérique et au violet de méthyle comme réactif colorant s'applique bien au dosage de l'antimoine, mais il est nécessaire d'employer le benzène, et non l'acétate d'amyle comme agent d'extraction; ce dernier risque en effet d'extraire le colorant lui-même.

SUMMARY

The oxidation technique using ceric sulphate and methyl violet as colouring reagent is very suitable for the determination of antimony, but it is necessary to use benzene and not amyl acetate as extraction medium, since the latter tends to extract the coloration itself.

ZUSAMMENFASSUNG

Die Methode der Oxydation mit Cerisulfat und Methylviolett als Farbreagenz ist gut zur Bestimmung von Antimon anwendbar, aber es ist dabei nötig Benzol und nicht Amylacetat als Extraktionsmittel anzuwenden, denn letzteres bewirkt eine Extraktion des Farbstoffes selbst.

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HETEROMETRIC MICRO-DETERMINATION OF URANIUM(VI) BY PRECIPITATION WITH FERROUS CYANIDE

by

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The precipitation of uranium (VI) with potassium ferrocyanide and its gravimetric determination as $UO_2[Fe(CN)_6]$ is bound up with considerable difficulties. The dark red precipitate obtained is of very fine colloidal character and therefore undergoes adsorption. Although the gravimetric method would be one of the most sensitive, because of the difficulties involved, the intensity of the colour obtained is used for the determination instead of a gravimetric determination. The following heterometric method is based on the photometric determination of the optical density of the *precipitated* $UO_2[Fe(CN)_6]$.

In this work it was our purpose to make use of all the advantages presented by the gravimetric determination of uranium, but to avoid separation and weighing. As the following material shows, no difficulties whatsoever are encountered due to *possible adsorption phenomena, so long as the precipitate is not separated from the solution*. This feature makes the heterometric method especially useful and easy to carry out. We present here only the *analytical* aspects of the results obtained.

EXPERIMENTAL

All details concerning the Heterometer and the heterometric titrations are given elsewhere[1,6]. The chemicals used were all Baker analysed c.p. reagents. A red filter was used in all the following experiments in order to avoid colour interference.

RESULTS

A selection of results are compiled in Table I and Figs. 1 and 2. The table gives the numerical values of the different experiments, while the curves show the course of titration of the corresponding experiments. The composition of each experiment is seen in Table I. By the dropwise addition of potassium ferrous

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cyanide to the solution of uranyl nitrate, we obtain in all cases without exception, a red brown *precipitate*, the optical density of which is measured. As experiment 1 and 3 show, under similar working conditions, we obtain the same numerical maximum density values in neutral and acidic solutions. The addition of NH_4NO_3 (exp. 2) increases the maximum value and therefore makes the measurements more sensitive. A comparison of exps. 4 and 5 shows that the titration with a more dilute ferrous cyanide solution causes some increase in the maximum density although less uranium is determined. But it must be borne in mind that even the maximum density value of the same experiment may vary somewhat with changing conditions (*e.g.* temperature etc.). The possible fluctuation of the maximum density value in no way impairs the accuracy of the determination, which does not depend on the numerical maximum value. For comparison, the experiments are grouped in two figures (1 and 2). As can be seen, the highest maximum values are obtained working in acid solution and at a high NH_4NO_3 concentration(exps. 7 and 8). The uranium concentration can then be reduced to about *one fifth* of the regular concentration used. As exp. 9 shows, a considerable decrease of the maximum value occurs in alcoholic solutions. In the presence of very high concentrations of NH_4NO_3, and with low concentration of uranium (exps. 7-9),

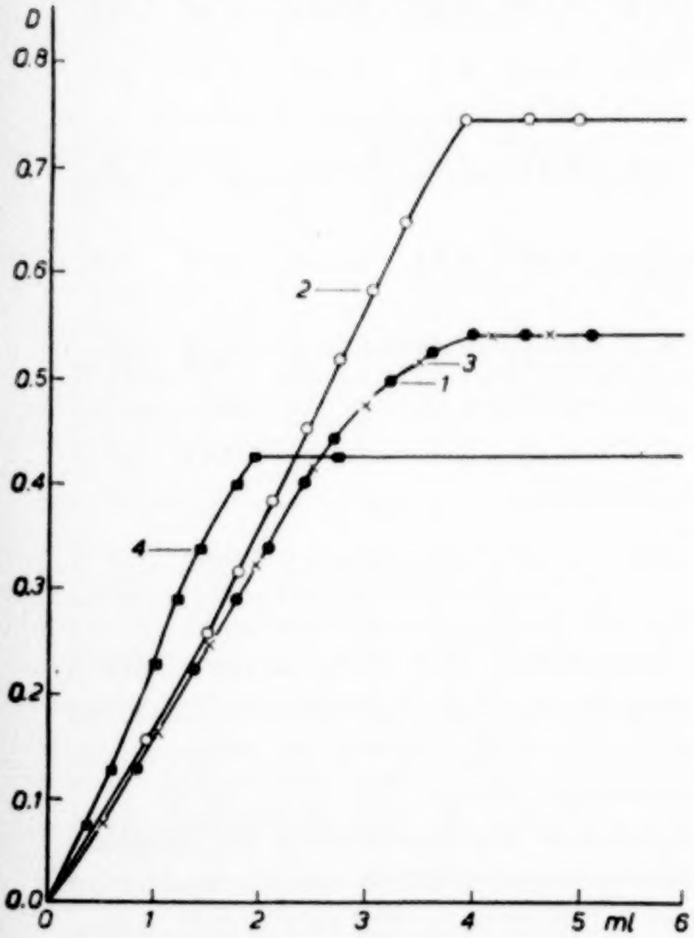

Fig 1.

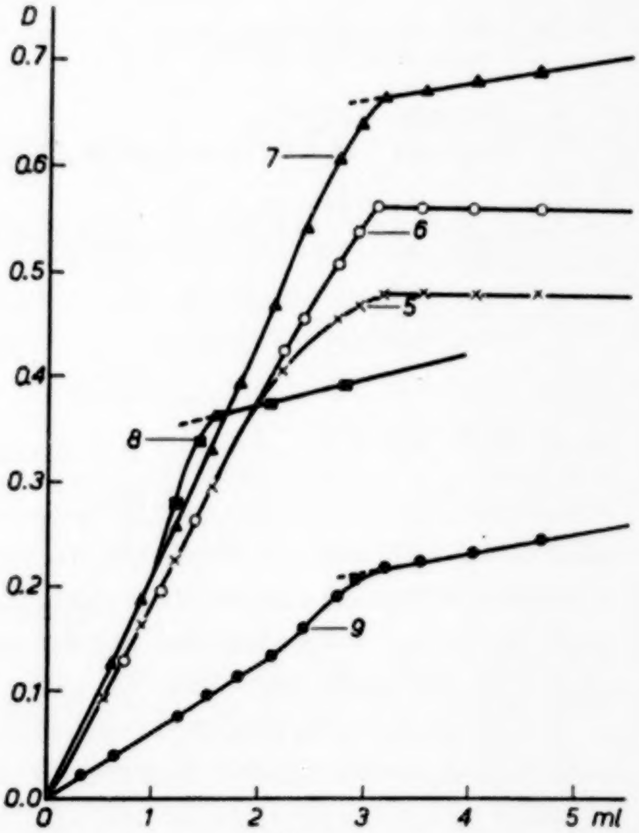

Fig. 2

TABLE I

General Composition: *a* ml n*M* $UO_2(NO_3)_2$ + (10-a) ml solution + X ml m*M* $K_4[Fe(CN)_6]$

Exp.	Solution	$UO_2(NO_3)_2$ ml	$UO_2(NO_3)_2$ molar	Uranium in mg	$K_4[Fe(CN)_6]$ used ml	$K_4[Fe(CN)_6]$ molar	Maximum density	% Error
1	6 ml H_2O	4	0.004	3.81	4.0	0.004	0.54	0
2	3 ml 1*M* NH_4NO_3 + 3 ml H_2O	4	0.004	3.81	3.9	0.004	0.75	2.5
3	1 ml 1*M* CH_3COOH + 5 ml H_2O	4	0.004	3.81	4.0	0.004	0.54	0
4	6 ml 1*M* NH_4NO_3	4	0.002	1.905	1.95	0.004	0.43	2.5
5	6 ml 1*M* NH_4NO_3 + 1 ml H_2O	3	0.002	1.43	3.1	0.002	0.48	3.3
6	6 ml 1*M* NH_4NO_3 + 1 ml 1*M* CH_3COOH	3	0.002	1.43	3.0	0.002	0.56	0
7	3 ml 6*M* NH_4NO_3 + 1 ml 1*M* CH_3COOH + 3 ml H_2O	3	0.002	1.43	3.05	0.002	0.68	1.6
8	3 ml 6*M* NH_4NO_3 + 1 ml 1*M* CH_3COOH + 3 ml H_2O	3	0.001	0.714	1.55	0.002	0.38	3.3
9	1 ml 1*M* CH_3COOH + 1 ml H_2O + 5 ml alcohol	3	0.002*)	1.43	3.0	0.002*)	0.23	0

*) 50% alcohol

the maximum density lines are no longer horizontal. The time required for a complete titration shows little variation, even though the uranium concentration and the other experimental conditions vary. Generally, about 20 minutes are required for each titration, at room temperature.

It now remains to clarify the interrelation between the *sensitivity* of the titration and the *accuracy* of the determination. The numerical value of the maximum density indicates to what extent an analysed solution may still be diluted, hence it indicates the sensitivity. This does not necessarily mean that the latter property is connected with the highest precision. The determination of the endpoint is easy and sure, given the following conditions: 1) the reaction proceeds quickly thus giving constant galvanometer readings after a few seconds; 2) the first maximum density value remains unchanged by the addition of titrant or the changes proceed regularly. The sensitivity, on the other hand, depends on the insolubility (expressed in mol.) of the compound obtained.

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METHOD

1-2 ml concentrated NH_4NO_3 and a few drops of concentrated acetic acid (final concentration about $0.1N$) are added to a water solution which contains a few mg of uranium (VI) (0.5 to 3 mg) in a volume of about 10 ml. A standardized solution of about $0.002M$ $K_4[Fe(CN)_6]$ is added drop by drop from a microburet while the solution is stirred vigorously. The readings of the galvanometer are taken when they become constant. The first maximum optical density point which corresponds to the endpoint, is taken by extrapolation from a graph (enlarged) by drawing a line through the maxima values obtained. Where the quantity of uranium is unknown, it is advisable to make a rough preliminary heterometric titration, taking only a few points, following which the final titration is made.

SUMMARY

A method is presented for the determination of uranium (VI) by a heterometric titration with $K_4[Fe(CN)_6]$. 0.5-3 mg of uranium in 10 ml solution may be determined in 15-20 minutes. The error amounts to 0-3%.

RÉSUMÉ

Une méthode est présentée pour la détermination de l'uranium (VI) au moyen de $K_4[Fe(CN)_6]$ par titration hétérométrique. 0.5-3 ml d'uranium dans 10 ml de solution peuvent être déterminés en 15-20 minutes, avec une erreur de 0-3%.

ZUSAMMENFASSUNG

Eine Methode wird gebracht zur Bestimmung von Uranium (VI) mit Hilfe einer heterometrischen Titration mit einer Lösung von $K_4[Fe(CN)_6]$. 0.5-3 mg Uranium in 10 ml Lösung können in 15-20 Minuten mit einer Genauigkeit von 0-3% bestimmt werden.

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THE POLAROGRAPHIC DETERMINATION OF ZINC AND MANGANESE IN PLANT AND ANIMAL TISSUES AND SOILS

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INTRODUCTION

Up to the present the polarograph has provided the most precise method for the estimation of zinc in biological materials. The colorimetric estimation of manganese by oxidation to the permanganate ion (WILLARD AND GREATHOUSE[25]), although very convenient, suffers somewhat in sensitivity, and although the various colorimetric methods[4,7,9,15] which depend essentially on the catalytic oxidation of various substituted dialkyl anilines to blue compounds are very sensitive, they lack specificity and precision by being somewhat empirical.

HAMAMOTO[10] showed that manganese may be estimated polarographically with great precision, while ZAK[26] demonstrated the versatility of the polarograph by estimating manganese, copper, zinc and antimony in samples of ashed lucerne. In many samples of natural products, zinc and manganese occur in concentrations of similar order and since the polarographic waves of these two metals when developed together in a number of supporting electrolytes are far enough apart to permit precise measurement, their simultaneous extraction and estimation may be accomplished conveniently.

For satisfactory polarographic measurements of zinc (—1.0 v) and manganese (—1.5 v), the requirements are freedom from nickel (—1.1 v), cobalt (—1.2 v), iron (—1.3 v) and aluminium (—1.75 v), with the $E_{\frac{1}{2}}$ values V S.C.E. in 0.1*N* LiCl solution in parenthesis. Various attempts have been made to suppress the interfering waves, but nothing short of the chemical separation of the extraneous metals has been really successful. A neutral supporting electrolyte is desirable, since if an acidic electrolyte is employed, the early rise of the hydrogen wave tends to distort the manganese wave.

HAMAMOTO[10] removed the iron and aluminium by precipitation as the basic acetates, precipitated the manganese as the hydrated manganic oxide and after solution in acid and evaporation, polarographed the manganous ion in a lithium chloride supporting electrolyte. This process is rather long and it was found that traces of zinc and manganese are adsorbed by the basic acetates.

With ZAK's[26] method, the ash of the lucerne was evaporated with hydrochloric acid to remove silica and the residue was dissolved in lithium chloride solution, filtered and then polarographed. Any aluminium and iron would hydrolyse in this neutral solution and the hydroxides would adsorb some zinc and manganese. The proposed method avoids these disadvantages by removing the iron by extraction with cupferron, and subsequently extracting the zinc and manganese with sodium diethyldithiocarbamate (D.D.C.) which does not extract aluminium. The two metals are thus freed from interfering elements, without precipitations and the consequent hazard of adsorption. The method may be applied to highly calcareous substances such as bone or milk products, animal tissues, bloods, plant materials or to soils which may contain appreciable quantities of iron or cobalt.

REAGENTS

Sodium diethyldithiocarbamate (*D.D.C.*). If sufficiently pure and free of Zn, Mn, Co and Fe, it may be used in the crystalline state. If impure, it may be prepared as a 1% aqueous solution, filtered and extracted with chloroform to remove these metals. If kept in a refrigerator the solution may be used for up to four days.

Dimethylglyoxime. 1% W/V solution in glass-distilled ethanol.

Chloroform. Good quality chloroform, washed with dilute sulphuric acid, refluxed over quicklime before distillation and stabilised by the addition of 1% ethanol.

Ammonium tartrate. 10% W/V aqueous solution extracted with D.D.C. and chloroform to remove any heavy metals.

Cupferron. 5% aqueous solution stored in a refrigerator will keep for up to two weeks.

Nitric, perchloric and sulphuric acids. All distilled from pyrex stills.

Ammonium hydroxide. Prepared by absorbing gaseous ammonia in glass-distilled water.

Bromocresol green indicator. 0.1% solution in glass-distilled ethanol.

Lithium chloride supporting electrolyte. 0.1M containing 0.005% gelatine. This solution should not be more than 10 days old, otherwise traces of acid from the oxidation of gelatine cause the hydrogen wave to distort the manganese wave.

Standard zinc solution. 1.438 g $ZnSO_4.7H_2O$ dissolved in 100 ml water acidified with 5 drops of hydrochloric acid. This produces 0.05M $ZnSO_4$ and the concentration of zinc should be checked gravimetrically after precipitation as $ZnNH_4PO_4$. 3.06 ml of this solution acidified with 5 drops of hydrochloric acid and diluted to 100 ml produces a solution containing 100 µg of zinc per ml.

Standard manganese solution. 0.05M manganese solution may be prepared by dissolving 0.791 g of pure $KMnO_4$ in water containing 10 drops concentrated sulphuric acid and bubbling sulphur dioxide until the solution is colourless. Excess sulphur dioxide is boiled off without loss of solution which is then made up to 100 ml. When 3.64 ml of this solution is acidified with 5 drops of hydrochloric acid and diluted to 100 ml, a standard is produced containing 100 μg of manganese per ml.

APPARATUS

A Sargent model XXI polarograph, employing Heyrovsky cells with mercury pool anodes is used. Pyrex glassware is used throughout. The removal of oxygen from the solutions is accomplished by bubbling nitrogen or hydrogen through them. The gas stream is purified by passage through a pair of wash bottles containing vanadyl sulphate reduced by nascent hydrogen as recommended by MEITES AND MEITES[19].

PROCEDURE

Depending on the quantity of manganese present, 1 to 2 g of oven-dried material are wet digested with nitric, perchloric and sulphuric acids and silica is removed by centrifugation. The digest is transferred to a separating funnel where it is diluted to 50 ml and the iron and copper are removed by extraction to exhaustion with cupferron and chloroform. This is followed by two washes with chloroform.

After the addition of 5 ml of ammonium tartrate solution and three drops of bromocresol green, ammonia solution is added until the indicator turns a definite blue (pH 5.5). Approximately 30 mg of crystalline D.D.C. (or 3 ml of 1% solution) is added and dissolved by shaking rapidly. 5 ml of chloroform are added, shaken for one minute and the solvent phase is run off into a test tube. A similar quantity of D.D.C. is again added, dissolved and the metal complexes are extracted with chloroform. This process is repeated until the solvent phase is colourless. Two such additions of D.D.C. are usually sufficient to extract all of the zinc and manganese.

The chloroform is distilled off from the extracts and the carbamates are decomposed by heating in the test tube to the charring stage with 8 drops of concentrated sulphuric acid and then adding 10-drop quantities of nitric acid and heating strongly until the decomposition of the organic matter is complete. The use of perchloric acid is avoided at this stage, as the last traces are often difficult to remove, and if any remains, distortion of the manganese wave occurs.

The solution is now transferred completely with rinsings to a 50 ml beaker from which the water is evaporated and the sulphuric acid is fumed off completely; the removal of the last traces of sulphuric acid is essential, otherwise the hydrogen wave distorts the manganese wave.

Ease of solution of the extracted metals is ensured by wetting the residue with a few drops of dilute hydrochloric acid and evaporating to dryness followed by a second and a third wetting with distilled water and drying to remove the last

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traces of hydrochloric acid. The metallic residue is finally dissolved in 3 ml of lithium chloride supporting electrolyte, transferred to the polarographic cell and after the removal of the oxygen the solution is polarographed between —0.8 v and —1.7 v. Within this span the waves of zinc (—1.0 v) and manganese (—1.5 v) develop and may be measured for comparison with those produced by known quantities of these metals.

Soil extracts may be treated in a similar manner once the organic matter has been oxidised, but any large quantity of iron should first be extracted with amyl acetate as suggested by WELLS AND HUNTER[24], then any remaining traces should be removed with cupferron.

In the case of samples containing appreciable quantities of cobalt and nickel, the extraction of zinc and manganese by D.D.C. may be performed at pH 9.5 after the addition of 5 ml of dimethylglyoxime solution and an extraction by chloroform to remove the nickel. This procedure is satisfactory for samples low in calcium. With highly calcareous soils it is safer to extract with D.D.C. at pH 5.5 at which reaction the calcium remains in solution, decompose the extract and then extract again at pH 9.5 in the presence of dimethylglyoxime. There is seldom enough cobalt or nickel in bones or milk products to warrant the double D.D.C. extraction.

DISCUSSION

In arriving at the final procedure, various chelating agents were tried for the extraction of zinc and manganese. The extraction of zinc is relatively simple and most of the investigation centred round the quantitative extraction of manganese. Very few chelating agents are suitable for manganese; MALEY AND MELLOR[17, 18] and IRVING AND WILLIAMS[11] have shown that the chelated compounds of manganese are considerably less stable than those of the other divalent transition metals. IRVING AND WILLIAMS[12] indicated that the order of relative stability of complexes with these metals holds, in general, for different reagents, and that competitive complexing by tartrate and citrate would be greater with manganese than with the other metals. With all the reagents quoted by FRIESER[8] manganese was low on the list of stabilities, but he pointed out that chelating agents containing sulphur tend to produce more stable compounds than do those in which the metal is linked through an oxygen atom.

While dithizone is an excellent extractant for zinc, it is not suitable for manganese as ~~the extr~~action even in the presence of acetate is far from complete. 8-Hydroxyquinoline is capable of extracting both zinc and manganese, but it also extracts aluminium. Furthermore it is frequently difficult to completely oxidise the organic matter of an oxine extraction in order to polarograph the metallic residue. Traces of nitropyridine which resist oxidation remain and distort the zinc and manganese waves.

Sodium diethyldithiocarbamate (D.D.C.) was selected as an extracting reagent since it reacts with both zinc and manganese forming colourless and rose pink complexes respectively, but it does not extract aluminium. Considerable work has been carried out with this reagent particularly in connection with the colorimetric estimation of copper, and although the interference offered by manganese to the estimation of copper has been referred to (COULSON[5], OVENSTON AND PARKER[20], DRABKIN[6]), and D.D.C. has been used to remove manganese prior to the estimation of uranium (SHORT[21]) and of calcium and magnesium (CHENG, MELSTED AND BRAY[2]), this reagent does not appear to have been used extensively for the extraction and estimation of manganese.

CHERNIKHOV AND DOBKINA[3] pointed out that for complete extraction of manganese an excess of D.D.C. is necessary. This is confirmed by the author, and it is in agreement with the expected property of manganese complexes considering the low order of stability of most of these chelated compounds. TOMPSETT[23] used D.D.C. to extract lead and prevented the extraction of copper and iron by the addition of cyanide. However with the excess D.D.C. required for the extraction of manganese, neither cyanide, citrate nor pyrophosphate is able to completely prevent the extraction of some iron. The diethyl ammonium diethyldithiocarbamate suggested by STRATFORD, WYATT AND KERSHAW[22] as an extractant for Group II metals was found to be less effective than D.D.C. for manganese because of the difficulty of attaining the necessary excess of reagent in the aqueous phase.

PURITY OF THE REAGENT

Numerous references in the literature point to the difficulties of obtaining the dithiocarbamates in a pure state, so it was essential that the effective purity of the D.D.C. available should be determined. A variation of the method of KARSTEN, RADEMAKER AND WALRAVEN[14] was employed, wherein the exact quantity (545 μg) of D.D.C. required to react stoichiometrically with 100 μg of copper to form $Cu(S.SCNEt_2)_2$ was added to each of several 100 ml flasks, together with a small quantity of gum arabic to keep the copper complex in the disperse state. To these were added graded quantities of copper from 30 μg to 125 μg.

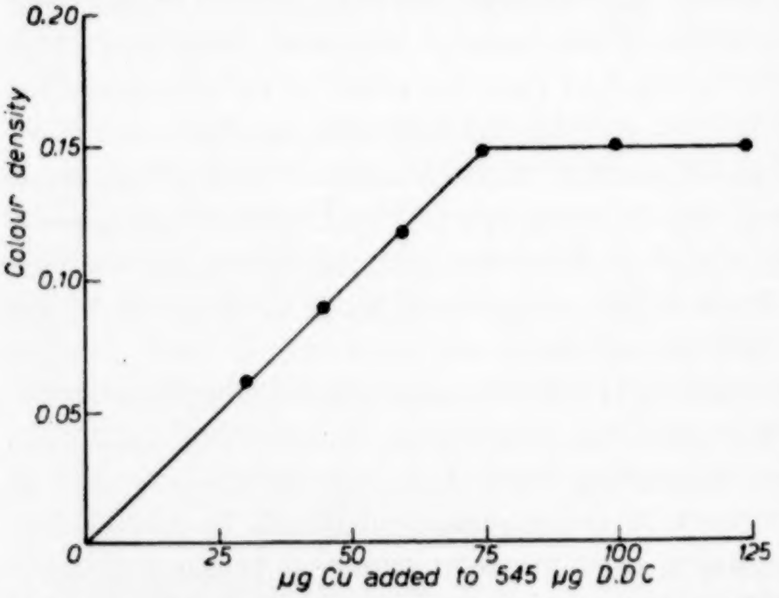

Fig. 1. Showing the determination of the effective purity of the D.D.C.

After the addition of ammonia the volumes were made up to 100 ml and the colour densities were measured in a spectrophotometer at 440 mμ. From these results depicted in Fig. 1 it was seen that only 75 μg of copper was complexed and that the effective purity of the reagent was 75 per cent. This figure was confirmed by adding the same quantity (545 μg) of D.D.C. to 1,000 μg of copper, extracting with chloroform, washing the solvent phase with water, evaporating the chloroform, decomposing the organic matter and estimating the extracted copper polarographically. Again, even in the presence of a large excess of copper only 75 μg were extracted by 545 μg of D.D.C. KARSTEN *et al.*[14] quote the composition of D.D.C. as being $Et_2NCS.SNa.3H_2O$; this corresponds to 76 per cent. of the anhydrous carbamate.

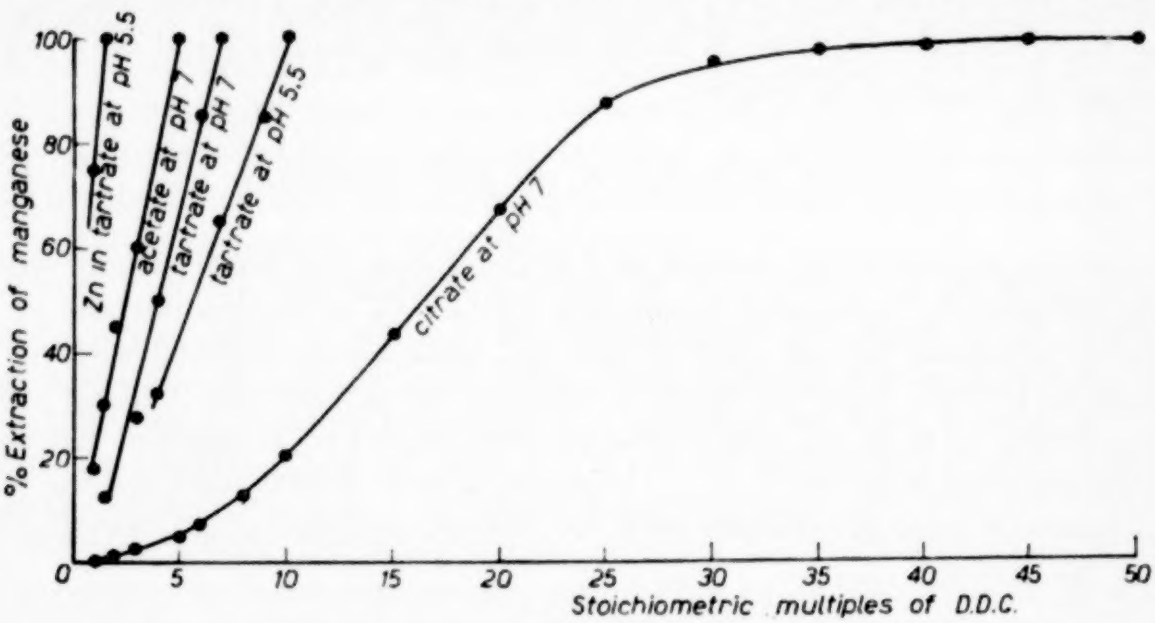

Fig. 2. Showing the percentage extraction of manganese in the presence of various stoichiometric multiples of D.D.C. when the solutions are buffered by acetate, tartrate and citrate.

COMPETITIVE COMPLEXING BY BUFFERS

With the effective purity of the D.D.C. established, it was then necessary to determine the extent of the excess of the reagent required for the complete extraction of zinc and manganese from solutions buffered with different buffering compounds. A reaction of pH 7 was selected, buffered with 0.5 g of ammonium acetate, ammonium tartrate and ammonium citrate in each case. To each solution was added 100 μg each of zinc or manganese, then various stoichiometric multiples of D.D.C., followed by extractions with three 5 ml portions of chloroform, with the extracted metals determined polarographically in each case.

At pH 7 zinc was extracted with stoichiometric quantities of D.D.C. in the presence of all of these three buffers, but with manganese in the presence of acetate, tartrate and citrate 5, 7, and 45 stoichiometric multiples respectively were required. These results are shown in Fig. 2.

Since tartrate buffered at pH 5.5 was later selected as a suitable medium for the extraction of these two metals, the extraction of zinc and manganese was examined under these conditions when it was found that zinc requires 1.5 and manganese requires 10 stoichiometric multiples of D.D.C. for complete extraction.

Of the three buffering compounds examined acetate gives a clear, rapid extraction of manganese, but in the presence of aluminium the basic acetate is precipitated at pH 4 and higher and the precipitate adsorbs some zinc and manganese. The digests of a series of legumes, buffered with acetate, gave slightly lower results for both zinc and manganese than did duplicate aliquots buffered with tartrate before extraction. Solutions buffered with citrate on the other hand require a great excess of D.D.C. and long shaking times. Tartrate was regarded as the most desirable because it keeps aluminium in solution and only requires a reasonable quantity of reagent.

EFFECT OF REACTION ON EXTRACTABILITY

The next question to be decided was to determine the most suitable reaction for the extraction of zinc and manganese by D.D.C. With this purpose in view solutions containing 100 μg each of zinc and manganese, buffered with 0.5 g of ammonium tartrate with the reaction adjusted to various values of pH and the volumes made up to 50 ml, were extracted with three 5 ml portions of chloroform after the addition of excess D.D.C. The extracts were decomposed and the metals were estimated polarographically with the results expressed graphically in Fig. 3, curves (a) and (b).

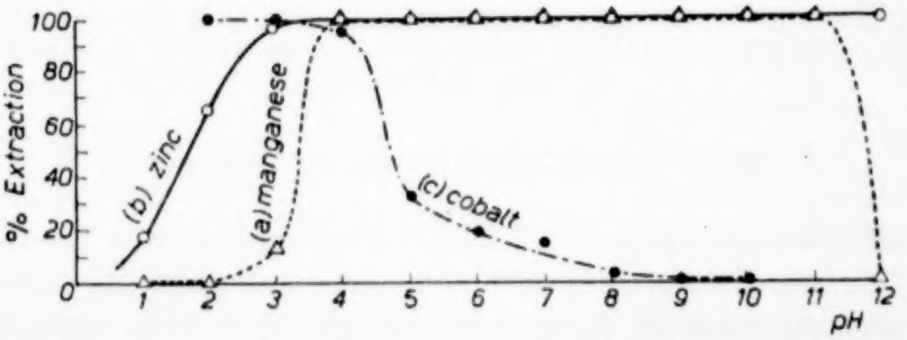

Fig. 3. Showing the extractability of zinc and manganese in the presence of tartrate, also the protection afforded to cobalt by dimethylglyoxime, as influenced by pH.
(a) Extraction of manganese by excess D.D.C. in the presence of tartrate.
(b) Extraction of zinc by excess D.D.C. in the presence of tartrate.
(c) Extraction of cobalt by D.D.C. in the presence of dimethylglyoxime and tartrate.

These indicate that with excess D.D.C. in the presence of tartrate, zinc is extracted completely between pH 3 and pH 12, while manganese under the same conditions is fully extracted between pH 4 and pH 11. In order to prevent the possibility of precipitation of calcium phosphate during the extraction a reaction of pH 5.5 was chosen; this may be conveniently reached by adding ammonia to the solution until bromocresol green indicator just turns blue. The extraction of manganese at pH 5.5 by excess D.D.C. was found not to be influenced by the prior addition of either hydroxylamine or bromine water.

INTERFERENCE BY COBALT AND NICKEL

LACOSTE, EARING AND WIBERLEY[16] examined the extraction and colorimetric estimation of several metals by means of D.D.C., and showed that cobalt and nickel are extractable over a wide range of reactions. Since the presence of these two metals would seriously interfere with the measurement of the zinc wave in lithium chloride supporting electrolyte, their absence in the final extract is essential. With plant products and biological samples, the concentrations of cobalt and nickel compared with those of zinc and manganese are so low that they can usually be disregarded and no precautions need be taken. However samples such as soils frequently contain appreciable quantities of cobalt and nickel so that steps must be taken to eliminate their interference.

The use of dimethylglyoxime is suitable for the removal of nickel and for the rendering of the cobalt insoluble in the solvent phase providing the pH is above 9 (BUTLER AND ALLEN[1], JONES[13]). This was demonstrated by extracting with excess D.D.C. solutions containing 100 μg each of cobalt, 5 ml of 1% dimethylglyoxime solution, 0.5 g tartrate and adjusted to various pH values and finally estimating the cobalt polarographically. The results depicted graphically in Fig. 3, curve (c), show that the cobalt dimethylglyoxime complex has sufficient stability above pH 9 to completely resist competitive complexing by D.D.C., that at pH 4.5 the stabilities of the two complexes are approximately equal, whereas at pH 3 and lower the stability of the glyoxime is much lower than that of the carbamate.

Thus in order to suppress the interference by cobalt and nickel, dimethylglyoxime should be added, the reaction raised to pH 9.5 and the solution should be extracted with chloroform to remove nickel. At the same time at this reaction the cobalt is rendered insoluble and the zinc and manganese may then be extracted with D.D.C. In the event of the sample containing cobalt or nickel being highly calcareous, the procedure found best is to make an initial extraction at pH 5.5 to avoid the precipitation of calcium, decompose the extract and then re-extract at pH 9.5 after treatment with dimethylglyoxime.

PRECISION OF THE METHOD

In order to demonstrate the precision of this method two samples of plant material were digested and aliquots of each were extracted and polarographed in quadruplicate. The samples were chosen to provide both low and high levels of manganese content, as it was felt that this metal is the more difficult to extract. The results found are set out in Table I.

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TABLE I

(a) Sample XF 1042 (bromus and barley grasses)		
(i)	11.5 p.p.m. Zn	23.2 p.p.m. Mn
(ii)	11.5 ,,	23.3 ,,
(iii)	11.6 ,,	23.6 ,,
(iv)	11.3 ,,	23.2 ,,
(b) Sample XF 1156 (Banksia marginata)		
(i)	13.6 p.p.m. Zn	755 p.p.m. Mn
(ii)	13.9 ,,	759 ,,
(iii)	13.6 ,,	755 ,,
(iv)	14.2 ,,	760 ,,

In order to select an aliquot suitable for the manganese estimations in the second sample the quantity of zinc was small, so that the precision for zinc suffered somewhat. Nevertheless the precision shown here is very satisfactory.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made of the helpful advice and interest of Mr. H. R. MARSTON, F.R.S., Chief of the Division of Biochemistry and General Nutrition, C.S.I.R.O., and of the technical assistance of Mr. J. S. CHARNOCK.

SUMMARY

A method is proposed whereby microgram quantities of zinc and manganese may be simultaneouly extracted with excess sodium diethyldithiocarbamate in the presence of tartrate at pH 5.5, the extracts decomposed and the metals polarographed in a lithium chloride supporting electrolyte. Iron must first be removed with cupferron, and the interference by cobalt and nickel is overcome by the use of dimethylglyoxime prior to the extraction. The method may be applied to the digests of animal tissues, plant materials or soils.

RÉSUMÉ

Une méthode est proposée pour l'extraction simultanée de microquantités de zinc et de manganèse, au moyen d'un excès de diéthyldithiocarbamate de sodium, en présence de tartrate, au pH 5.5; l'extrait obtenu est décomposé et les métaux sont polarographiés en présence de chlorure de lithium comme solution de base. Il est nécessaire, avant d'effectuer l'extraction, d'éliminer le fer par le cupferron, le cobalt et le nickel par la diméthylglyoxime. La méthode peut être appliquée aux tissus animaux, aux plantes et à la terre.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen mit der gleichzeitig Milligrammengen von Zink und Mangan mit einem Überschuss von Natriumdiäthyldithiocarbamat in Gegenwart von Tartrat bei pH 5.5 extrahiert werden können, die Auszüge zersetzt und die Metalle in einem Lithiumchlorid tragenden Elektrolyten polarographiert werden können. Eisen muss zuerst mit Cupferron entfernt werden und die durch Kobalt und Nickel hervorgerufene Störung wird durch die Anwendung von Dimethylglyoxim vor der Extraktion ausgeschaltet. Die Methode kann auf digerierte tierische Gewebe, Pflanzenmaterialien und Böden angewandt werden.

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REVUE DE LIVRES

Starch and its Derivatives, de J. A. Radley, M.Sc., F.R.I.C. Volume I, 3ème édition, Chapman & Hall Ltd., London 1953, 510 pages, 37 tableaux, 19 figures, 65*s*.

Ce prémier volume donne une excellente vue d'ensemble sur la chimie actuelle de l'amidon. La première partie se compose d'une série d'articles de différents auteurs. Radley s'est assuré la collaboration de spécialistes renommés.

Après un bref aperçu historique, le lecteur est mis au courant des problèmes les plus importants de cette branche de la chimie: fonctions biologiques de l'amidon, action des enzymes (dégradation et synthèse, etc.).

Des références nombreuses, des tableaux clairs, des photographies intéressantes, augmentent encore l'intérêt de cet ouvrage. Un autre avantage de ce livre réside dans le fait qu'à côté de théories purement scientifiques, on trouve l'exposé de procédés techniques.

Principaux sujets traités: structure de l'amidon en amylose et en amylopectine, caractérisation de ces produits basée sur les travaux de K. H. Meyer, Staudinger, Hassid, Freudenberg et d'autres encore; schémas de réaction de dégradation par méthylation suivie d'une hydrolyse acide, et dégradation par $NaIO_4$; recherches sur les fractions de l'amidon, propriétés physiques, gonflement, rayons X, gélatinisation, etc.; analyses spectrophotométriques de l'amidon en présence d'iode, mécanisme et sensibilité de cette réaction, ses anomalies, dextrinisation, formation d'esters et d'éthers, leurs dérivés inorganiques, l'oxydation, la réaction à la formaldéhyde.

La deuxième partie de cet ouvrage est réservée aux enzymes amylolytiques, principalement aux α- et β-amylases. On y décrit leur purification, leur action sur l'amidon, leurs propriétés et leur cinétique, etc.

A ce livre, par ailleurs extrêmement intéressant et complet, il faut faire une légère restriction: certains phénomènes sont répétés plusieurs fois, ce qui alourdit un peu la matière. Mais la valeur primordiale de cet ouvrage consiste surtout en ce que l'auteur ne se contente pas de faire une compilation des recherches effectuées jusqu'à ce jour, mais en fait une analyse critique approfondie.

H. Hilpert (Genève)

Starch and its Derivatives, de J. A. Radley, M.Sc., F.R.I.C. Volume II, 3ème édition, Chapman & Hall Ltd. London 1953, 465 pages, 20 graphiques, 25 tableaux, 49 microphotographies, 65*s*.

C'est le rôle joué dans l'industrie par l'amidon et ses produits qui est traité dans ce deuxième volume. Les trois parties dont il se compose décrivent la manufacture, l'application industrielle et l'analyse de l'amidon.

Comme pour le 1er volume, il se compose aussi d'une série d'articles écrits par des spécialistes sur le problème de la fermentation, les méthodes physiques et en général sur les caractéristiques de l'amidon.

Ce volume est illustré d'un grand nombre de photos d'équipements industriels, de microphotographies, de tableaux.

Après avoir examiné l'importance commerciale de l'amidon, du blé, du riz et de l'amidon de sago, l'auteur nous donne une description détaillée de la manufacture du maïs, du glucose et du maltose. Puis un chapitre est consacré aux différents produits à base d'amidon: acétone, acide lactique, etc.

Il étudie avec soin l'application de méthodes physiques, tel que le traitement de l'amidon par la soude caustique, par des substances alcalines, par des acides, sels, oxydants et par des agents de gonflement.

Les chapitres concernant le côté tout à fait pratique sont intéressants: L'industrie des produits de la pomme de terre, la question de la couleur des "chips", la gélatinisation de l'amidon, le rôle de la diastase dans la farine, le phénomène de la cuisson du pain, la constitution du vieux pain, sont des titres de chapitres qui montrent le rôle de l'amidon dans la vie quotidienne.

On trouve encore la description de produits secondaires résultant de la fabrication de textiles et du papier. Et, pour terminer, ce livre très intéressant, le lecteur est initié aux déterminations analytiques de l'amidon et des dextrines et aux méthodes de caractérisation générale de l'amidon.

H. HILPERT (Genève)

Einführung in das Kunststoffgebiet von W. SCHAEFER, 2e éd. revue et augmentée. XV, 594 pages. Akademische Verlagsgesellschaft Geest & Portig K.-G. Leipzig 1953. Relié 30 DM.

Le succès remporté par cet ouvrage a obligé l'auteur à faire paraître la seconde édition moins de deux ans après la première. Il l'a complétée par la littérature parue entre 1950 et 1952. De nouveaux chapitres concernent les résines araldites, furaniques, polyéthers et éthoxylines. D'autres, se rapportant aux résines polyesters, à l'influence des substituants sur la polymérisation, à la polymérisation dite ,,à froid", aux relations entre les propriétés des matériaux synthétiques et la constitution des molécules, aux fluoroéthylènes et polyéthylènes, ont été complétés.

Les fibres synthétiques nouvelles, — Dynel et Terylène —, sont également décrites, alors que des détails supplémentaires sont fournis sur le Vinyon, l'Orlon et les fibres de verre. Rappelons que cet ouvrage comprend les parties suivantes:

a. la chimie des hauts polymères.
b. la physique des hauts polymères.
c. les matériaux de synthèse du commerce.
d. les fibres synthétiques.
e. les produits à base de matériaux de synthèse.
f. l'emploi des matériaux de synthèse.
g. contrôle chimique.
h. contrôle physique.

Il se termine par une liste fort utile des dénominations commerciales des matériaux de synthèse et d'une tabelle des formules de constitution de quelques résines synthétiques importantes.

C. HERSCHMANN (Genève)

L'analyse Chimique, par C. DUVAL, Presses Universitaires de France. Paris, 1953. 128 pages, 67 figures.

La collection "Que sais-je?" vient de s'enricher d'un magnifique ouvrage (No. 189) sur l'Analyse Chimique moderne, dû au Prof. Dr. C. DUVAL. Cet auteur a su unier la simplicité d'expression et la brièveté, avec la rigueur scientifique pour exposer avec clarté le développement actuel de l'analyse chimique. Cet ouvrage peut être utile à tous les lecteurs non spécialisés, désirant s'initier à la chimie analytique. Il est divisé en deux parties consacrées respectivement à l'analyse quantitative et qualitative. Il est complété par une courte introduction et une bibliographie. L'auteur expose les bases des techniques analytiques modernes, spécialement les méthodes instrumentales, sans décrire les réactions analytiques et les réactifs des cations et des anions, ni les applications pratiques des méthodes quantitatives. Nous félicitons M. le Professeur DUVAL pour la publication de cet intéressant ouvrage.

F. BURRIEL MARTÍ (Madrid)

Current Chemical Papers, publié par The Chemical Society, Burlington House, London, abonnement annuel (pour l'Europe) £ 2.10 ($ 7.50); pour les autres destinations, envoi par avion: £ 4.5 ($ 12.75).

Nous avons le plaisir d'informer nos lecteurs de la parution d'une nouvelle revue bibliographique: "Current chemical papers". Cette revue, qui paraîtra tous les mois, donnera la liste des principaux articles parus (reçus dans le courant du mois précédent), le nom des auteurs, la référence au journal original. Cette bibliographie qui ne pourra évidemment pas être complète, a pour but de renseigner les chimistes plus rapidement que ne peut le faire les Abstracts.

Y. RUSCONI (Genève)

SYMPOSIUM ON MICROCHEMISTRY AND MICROCHEMICAL INSTRUMENTATION

September 17, 1954, at Convention Hall, Philadelphia, Pa.

A Symposium on Microchemistry and Microchemical Techniques will be held on September 17, 1954 in connection with the I.S.A. First International Instrument Exposition, at Convention Hall in Philadelphia. The purpose of the Symposium is to show that Microchemistry has now come of age and supplies a useful and much needed technique. Historical development and newest progress in various phases will be presented with emphasis on instrumentation. The Symposium should serve as a review of past and present accomplishments as well as an idea of what may be expected in the future.

Program

9:30 A.M.	Opening of Symposium and introductory remarks by Chairman, H. K. Alber, Arthur H. Thomas Co., Philadelphia, Pa.
10:00 A.M.	Lecture of Honorary Chairman of Symposium, A.A. Benedetti-Pichler, Queens College, Flushing N.Y., *Microchemical Techniques.*
10:50 A.M.	Discussion and introduction of next speaker.
11:00 A.M.	Al Steyermark, Hoffmann-LaRoche, Inc., Nutley, *Quantitative Organic Microanalysis.*
11:00 A.M.	Discussion and lunch recess.
2:00 P.M.	Introductory Remarks and next lecture.
2:10 P.M.	John Mitchell, Jr., E. I. DuPont Co., Experiment Station, Wilmington, Delaware, *Physico-Chemical Methods in Microanalysis.*
2:50 P.M.	Discussion and introduction to next lecture.
3:00 P.M.	Harry Loving, Texas Oil Co., Beacon, N.Y., *Microanalysis in the Petroleum Industry.*
3:50 P.M.	Discussion and introduction to next lecture.
4:00 P.M.	Walter C. McCrone, Armour Research Foundation, Chicago, Ill., *Chemical Microscopy (Fusion Methods).*
4:50 P.M.	Discussion and showing of moving pictures depicting microchemical techniques (details to be announced later).

Committee for above Symposium consists of:

Arthur H. Hale representing the Affiliated Analytical Group, Delaware Section, A.C.S.
Jos. Alicine representing the Metropolitan Microchemical Society, N.Y.
Wm. C. Ellenbogen representing the Analytical and Microchemical Group, Philadelphia Section, A.C.S.
Richard Zahner representing the South Jersey Section, A.C.S.
Herbert K. Alber, *Chairman.*

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STRUCTURE AND BEHAVIOR OF ORGANIC ANALYTICAL REAGENTS

V. DIMETHYLGLYOXIME AND ITS OXYGEN MONOMETHYL ETHER*, **, ***

by

ROBERT G. CHARLES**** AND HENRY FREISER

Contribution of the Department of Chemistry, University of Pittsburgh (U.S.A.)

A comparison of the existing stability data for the reaction of a given chelating agent with a series of metal ions[2,3] shows that the stability order for a given reagent is much the same from reagent to reagent, although the individual metal chelate stabilities vary widely. The question of whether this general stability order is characteristic of all reagents is of considerable importance in determining the factors which confer selectivity or specificity upon a reagent. One of the most specific of all organic analytical reagents is dimethylglyoxime, which, under ordinary conditions, forms water-insoluble precipitates only with nickel (II) and palladium (II) ions. It was therefore thought desirable to investigate the stabilities of the chelates of this reagent by means of the Calvin-Bjerrum titration technique, in order to learn whether the famed specificity of this reagent for nickel is due to an unusually great stability of the nickel complex, relative to the stabilities of the other metal dimethylglyoxime complexes, or whether some other factor is involved.

Stability measurements were also extended to the chelates of the O-monomethyl ether of dimethylglyoxime. This compound is of particular interest since the structure of the nickel salt of dimethylglyoxime is known to involve hydrogen bonding[4,5], while no such hydrogen bonding is possible with the O-ether complexes.

EXPERIMENTAL

Materials. Baker and Adamson Reagent Grade dimethylglyoxime was recrystallized twice from ethanol-water mixtures and was dried in a vacuum desiccator.

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[*] For paper IV see reference (1).

[**] Abstracted from the thesis submitted by ROBERT G. CHARLES in partial fulfillment of the requirements for the Ph.D. degree in chemistry, August 1952.

[***] Taken in part from a paper presented at the Pittsburgh Conference of Analytical Chemistry and Applied Spectroscopy, March 1951.

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The O-monomethyl ether of dimethylglyoxime, prepared by the procedure of THILO[6], was supplied in generous amount by Mr. ALBERT C. HOLLER of Twin City Testing Laboratory of St. Paul, Minnesota. It was further purified by recrystallization from ethanol-water and dried under vacuum.

The other reagents employed have been described in the first paper of this series[7].

Apparatus and Procedure. The titration apparatus and general procedure have been described previously[7]. Values of K_{OH}, the acid dissociation constants of the reagents, were obtained in the usual fashion, by titrating the reagents with standard sodium hydroxide, in the absence of added metal salts. Since the two reagents are very weak acids it was found best to titrate a relatively high concentration of reagent (about $0.1M$) with the $0.1M$ NaOH solution, taking pH readings, only along the first tenth of the titration curve. By so doing, very high pH readings, which are more likely to be in error, are avoided, and any possible interference from the titration of a second hydrogen per reagent molecule (for dimethylglyoxime) is minimized. Over this range, both reagents were found to behave as monobasic acids. Similar titrations of the reagents in the presence of acid, in the usual fashion[7], showed that both have immeasurably small basicities ($pK_{NH} < 2$).

The titrations in the presence of metal ions[7] were modified in some instances by omitting the perchloric acid. Results obtained under these conditions were found to check closely with values obtained from titrations in the presence of acid. Because of the weak acidity of the reagents, and the resulting low concentration of reagent anion present at low pH values, it was necessary with a number of metal ions to use the largest possible concentration of reagent in order to keep the pH region of chelate formation below that of metal ion hydrolysis[7]. Even under these conditions hydrolysis occurred in certain instances, as indicated in the discussion portion of this paper.

All pH readings were corrected in the manner described in paper IV[1].

Calculations of Results. Formation constants were calculated in the manner described in Paper I. In the present work, as in previous papers of this series, it was assumed that the values of pR at $\overline{n} = 0.5$ and 1.5 represent $\log K_1$ and $\log K_2$, respectively.[*] This can be shown to be a good approximation when the values of pR at $\overline{n} = 0.5$

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[*] Where, as before[10], $\overline{n}$ is the average number of bound reagent anions per metal ion, pR is the negative logarithm of the monovalent reagent anion concentration, and K_1 and K_2, for chelates derived from divalent metal ions, are defined by:

$$K_1 = \frac{(MR^+)}{(M^{+2})\ (R^-)}\,,\quad K_2 = \frac{(MR_2)}{(MR^+)\ (R^-)}\,,\quad K_{av} = \sqrt{K_1 K_2}\,\sqrt{K_f}$$

corresponding to the reactions:

$$M^{+2} + R^- \overset{K_1}{\rightleftharpoons} MR^+$$

$$MR^+ + R^- \overset{K_2}{\rightleftharpoons} MR_2$$

$$M^{+2} + 2R^- \overset{K_f}{\rightleftharpoons} MR_2$$

and 1.5 are not too close together (a difference of about one logarithm unit is sufficient[8,9]). In the case of the Cu(II), Ni(II), and Co(II) chelates of dimethylglyoxime, the difference between the pR^- values, at $\bar{n} = 0.5$ and 1.5, were found to be unusually small. For calculation of absolute constants, in such cases, other terms are necessary, which may be applied in the form of a correction to the pR values[8]. For differences as small as those found for the copper, nickel, and cobalt chelates such corrections may be of appreciable magnitude. The nature of these corrections is such, however, that they are strongly affected by small errors in the pR values when the differences are as small as those observed in the present work, introducing considerable uncertainty into the correction to be applied. In view of these uncertainties we did not feel justified in applying corrections. The effect of these corrections would be to decrease the value of log K_1 and to increase the value of log K_2 for the complexes affected. This would in no way invalidate the conclusions reached below, but would rather magnify the effects observed.

It should be noted that in no case is a correction necessary for obtaining the value of log K_{av}, this value being obtained directly in all cases, either from the value of pR at $\bar{n} = 1$ or from the average of the pR values at $\bar{n} = 0.5$ and 1.5. The values of K_{av} in such cases are therefore known with greater accuracy than are K_1 and K_2.

Heat content changes and entropy changes for the reaction

$$2R^- + M^{+2} \xrightleftharpoons{K_f = (K_{av})^2} MR_2$$

where M^{+2} is Cu^{+2} or Ni^{+2}, were calculated in the usual manner, using values for the overall constants K_f at the temperatures 25° C and 40° C, and the equations:

$$\Delta F = -RT \ln K_f$$

$$\frac{d \ln K_f}{dT} = \frac{\Delta H}{RT^2}$$

$$\Delta F = \Delta H - T\Delta S$$

Results. The negative logarithm of the acid dissociation constant K_{OH}[7] for dimethylglyoxime was found to be 12.84 at 25.0° C and 12.45 at 39.6° C. The value of pK_{OH} for the O-monomethyl ether of dimethylglyoxime was found to be 12.92 at 25.0° C. The values of pK_{NH}, the negative logarithms of the acid dissociation constants for the protonated forms of the reagent[7], were found to be less than 2.0 for both compounds, indicating negligible basicity of the oxime nitrogen atoms.

Stability constants, calculated on the basis of the structures discussed below, are collected in Table I. Values for heat content and entropy changes are given in Table II.

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* Complete tables of experimental data are included in reference 10.

TABLE I

SUMMARY OF CHELATE FORMATION CONSTANTS

Dimethylglyoxime	Excess reagent	log K_1	log K_2	log K_{av}**	Temperature (°C)
Cu (II)	3-fold	11.94	11.36	11.66 11.65*	24.9
	5-fold	12.00	11.44	11.72 11.72*	25.2
	3-fold	11.68	11.07	11.39 11.38*	39.5
	5-fold	11.80	11.22	11.51 11.51*	39.6
Ni (II)	7.5-fold	11.09	10.49*	10.79	25.0
	12.5-fold	11.16	10.54	10.84 10.85*	25.2
	7.5-fold	11.10	10.50	10.81 10.80*	39.5
	12.5-fold	11.18	10.59	10.89 10.89*	39.6
		10.44	9.71	10.05 10.08*	25.0
Zn (II)	100-fold	7.7†	6.2†	6.4†	25.0
Pb (II)	100-fold	7.3	—	—	25.0
Cd (II)	100-fold	5.7†	5.0*†	5.3†	25.0
La (III)	64-fold	6.6†	5.9†	(log K^3 = 4.9†)	25.0

* refers to the calculation of the value so designated from the other two constants listed rather than by direct observation of the $\bar{n}$ vs pR curve[7].

** log K_{av} = 1/2 log K_f = 1/2 (log K_1 + log K_2)

Agreement between the observed and calculated values of log K_{av} is a measure of the internal consistency of the data.

† maximum value, obtained in the pH region of metal ion hydrolysis. See text.

TABLE I
(CONT.)

O-Monomethyl ether of dimethylglyoxime	Excess reagent	log K_1	log K_2	log K_{av}**	Temperature (°C)
Cu (II)	100-fold	9.5	6.6	9.2 8.1*	25.0
Ni (II)	100-fold	6.38	5.69	6.05 6.04*	25.0
Mn (II)	100-fold	6.18	5.42*	5.80	25.0
Zn (II)	100-fold	7.47	6.89	7.18 7.18*	25.0
Cd (II)	100-fold	6.3†	5.2†	5.5† 5.8*†	25.0

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TABLE II

ENTROPY AND HEAT CONTENT CHANGES INVOLVED IN CHELATION OF DIMETHYLGLYOXIME WITH COPPER (II) AND NICKEL (II) IONS

Metal	ΔS	ΔH
Copper (II)		
3-fold excess reagent	53.8 e.u.	—15.8 kcal.
5-fold excess reagent	76.1 e.u.	—12.0 kcal.
	mean 60.5 e.u.	—13.9 kcal.
Nickel (II)		
7.5-fold excess reagent	107.3 e.u.	+1.2 kcal.
12.5-fold excess reagent	105.6 e.u.	+2.9 kcal.
	mean 106.5 e.u.	+2.1 kcal.

DISCUSSION OF RESULTS

In the first series of titrations with dimethylglyoxime the reagent was present in three-fold excess. Under these conditions only the ions Cu (II), Ni (II), Co (II), and Zn (II) were found to form complexes. Titrations in the presence of the other metals gave curves that were identical to the hydrolysis curves obtained in the absence of reagent, and precipitates of the hydroxides were formed[7]. In a second series of titrations, using one hundred-fold excess of the reagent, complexes were found to form with Pb (II), Cd (II), and La (III) also, as indicated by the absence of precipitation during at least a part of the respective titrations. It is evident that, in these cases, a large excess of reagent is necessary to lower the pH region of complex formation below that of metal ion hydrolysis. At lower concentrations of reagent, the metal ion is removed from solution, as the hydroxide, before the pH is high enough for chelate formation to take place. It is probably true that a number of other metal ions would be found to form complexes with dimethylglyoxime if a sufficiently high concentration of reagent could be employed. In all of the titrations where complex formation took place, a total of two hydrogen ions were released during the titration, for each divalent metal ion, and three were released for La (III).

In the case of Cu (II), Ni (II), and Co (II) the dimethylglyoxime chelates are known to be of the type MR_2[11,12,13,14,*] and all the chelate formation takes place at pH values well below the pH region of metal hydrolysis, so that no difficulty is

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[*] In the discussion, HR refers to dimethylglyoxime and R^- to the reagent anion derived through the loss of one hydrogen ion per reagent molecule. The symbol D^{-2} is used to denote the anion derived through the loss of both of the two ionizable hydroxyl hydrogens of dimethylglyoxime. M represents the metal ion in question.

encountered in calculating formation constants for these complexes[7]. For the other metal ions studied, however, there are certain difficulties involved. In order for the equations derived in paper I to apply[7], it is necessary that the metal ion replace only one hydrogen ion from each reagent molecule with which it combines. In the case of the Pb (II), Zn (II), Cd (II), and La (III) complexes, with dimethylglyoxime, nothing is known concerning the respective structures. Since dimethylglyoxime has two potentially ionizable hydroxyl hydrogens, complexes of the type MD may be possible in certain instances. In addition, complexes of the type MROH may be possible for the divalent metals when the chelate formation takes place in the pH region of metal ion hydrolysis. $MROH^+$, MR_2OH, and $MR(OH)_2$ are similar possibilities for La (III), all of the above giving rise to the observed number of released hydrogen ions. The release of hydrogen ions during the titration precludes the formation of simple complexes involving only coordination through the oxime nitrogen atoms.

In the present work constants have been calculated on the assumption that the divalent complexes are of the type MR_2, and the La (III) complex of the type MR_3. These structures seem likely in view of (1) the similarity between the titration and pR vs $\bar{n}$ curves[10] with those of the Cu (II), Ni (II), and Co (II) chelates; and (2) the fact that the large monovalent cation MR^+ initially formed, would seem to be more likely to combine further with an R^- ion than with an OH^-, the hydrolysis of such large cations usually occurring only at comparatively high pH values. In addition there seems to be little or no evidence in the literature for complexes of the type MD with dimethylglyoxime. In the case of the lanthanum complex there is some precedent for the structure LaR_3 since the iron (III) ion is reported to combine with three dimethylglyoxime molecules[14].

In addition to the factors above, it should be noted that those values obtained in the pH region of metal hydrolysis must, in any event, be considered maximum rather than true values, due to the presence of metal species such as MOH^+, which were not taken into account in the derivation of equations for $\bar{n}$ and pR[7]. Values obtained under these conditions have been so marked in Table I, and have been included for purposes of comparison only.

Since the O-monomethyl ether of dimethylglyoxime has only one ionizable hydrogen, complexes of the type MD are excluded, and for those complexes which form at pH values below the region of metal ion hydrolysis, the structure must be of the type MR_2. Although several of the titrations occurred at rather high pH values, only the Cd (II) titration is believed to be seriously affected by hydrolysis.

The most striking fact to be noted by a comparison of the stability constants obtained with dimethylglyoxime is that the nickel complex is not the most stable, the order of decreasing stability being $Cu(II) > Ni(II) > Co(II) > Zn(II)$. This is essentially the same order that has been found for other reagents and indicates that the specificity of dimethylglyoxime for nickel must be due to some other cause, most likely to a difference in solubility. While the stability order is

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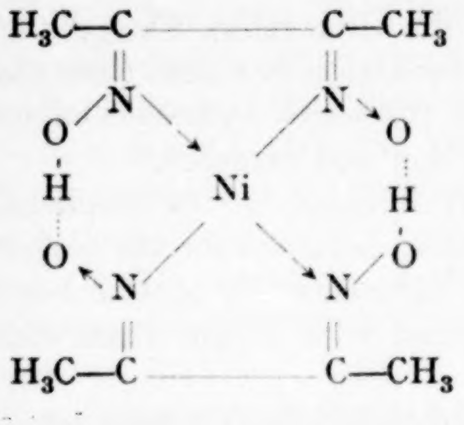

the same, an important difference seems to be that the three transition elements Cu(II), Ni(II), and Co(II), appear to form a group, with a rather large gap between the stabilities of these three and Zn(II). This seems to indicate that those metals with orbitals available for forming coplanar dsp^2 bonds give much the more stable complexes. The nickel complex of dimethylglyoxime has been shown to have the attached symmetrical coplanar structure. in which the remaining oxime hydrogens appear to be equally shared between two atoms[4,5]. It appears likely from the comparable stability of the complexes and from the similarity of the $\bar{n}$ vs pR curves[10] for the three compounds, that the Cu (II) and Co (II) chelates have similar structures to that of the nickel complex. In such a case the Cu and Co chelates might well have the same type of internal hydrogen bonding as the nickel complex[4,5], as has been drawn above. A fact which seems to point to the presence of strong internal hydrogen bonding in all three chelates is the comparatively small ratio of K_1/K_2. For most chelates so far investigated* log K_1 has been larger than log K_2 by about one unit. In the present case the difference is considerably lower than usual and, if the convergence corrections[8] referred to above were applied, this effect would be magnified. This seems to indicate that there is a stabilizing factor operating in the formation of the complex MR_2 which is not present in the initially formed MR^+. It is tempting to assume that this is due to the presence of strong internal hydrogen bonding in all three cases. Proof of this hypothesis must await additional evidence.

It should be mentioned that complexes of dimethylglyoxime with trivalent cobalt are also known, in addition to that with the divalent, and indeed some difficulty with oxidation was encountered in the cobalt-dimethylglyoxime titrations, despite the precautions taken. The data presented is from the best of several titrations and is believed to represent accurately the formation of the divalent complex.

The heat content and entropy changes occurring during chelation with dimethylglyoxime are of some interest (Table II). These results indicate that, especially for the nickel (II) complex, the driving force of the chelate formation is derived, in large measure, from the increase in entropy rather than from increases in bond strength. The rather large $\triangle S$ values are of the same order of magnitude as that found by CALVIN AND MELCHIOR[15] for the reaction of sodium 5-salicylaldehyde sulfonate with copper (II) in aqueous medium. CALVIN attributed this large value (100 e.u.) to the overall increase in the number of particles accompanying the reaction. It seems probable that a substantial portion of the entropy increase found here for the copper and nickel salts is due to the same cause. The greater value of $\triangle S$ for nickel over that found for copper probably arises both from the greater degree of hydration of the Ni (II) ion and the lesser hydration of its chelate, with respect to the corresponding Cu (II) ion and complex.

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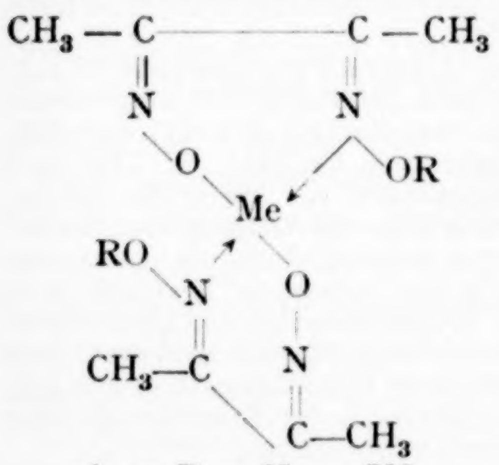
* See previous papers of this series and reference (2).

It is also significant to compare the value of $\triangle H$ obtained for the reactions. If the greater part of the difference between the values obtained for the copper and nickel chelates can be assumed to be due to differences in chelate bond strength, it is evident that stronger bonds are formed with copper than with nickel.

Since the hydrogen bonding discussed for the dimethylglyoxime chelates would be eliminated in the chelates of O-monomethyl ether of dimethylglyoxime, these were studied. It will be noted that the O-ether has nearly the same acid dissociation constant as dimethylglyoxime, as would be expected. Also like dimethylglyoxime, the O-ether has no measurable basicity.

A comparison of the stability constants of the O-ether with those of dimethylglyoxime show a number of significant differences. First, the complexes of Cu (II), and Ni (II) with the O-ether are of lower stability than the corresponding dimethylglyoxime chelates, while the reverse is true with the Cd (II) and Zn (II) complexes. Second, the order of decreasing stability for the complexes of the O-methyl ether was found to be Cu (II) > Zn (II) > Ni (II) > Mn (II) > Cd (II). This order differs considerably from that reported for dimethylglyoxime, particularly with respect to nickel which is scarcely more stable than manganese with the O-ether. Calculations for the cobalt complex indicate that it is more stable than the copper chelate. In this case it may be that the cobalt is oxidized to give a trivalent complex of the type CoR_2^+, rather than the expected divalent complex CoR_2, despite the precautions taken, since complexes of the former type are known for dimethylglyoxime. The titration data could not distinguish between this possibility and the divalent complex since two hydrogen ions per metal ion would be released in either case. The argument for this possibility is strengthened by the fact that a peculiarly shaped formation curve results from plotting the titration data[10]. Because of this uncertainty, constants for the cobalt complex are not included in Table I.

At least two factors must be considered in explaining the behavior of the O-monomethyl ether of dimethylglyoxime: (1) the absence of hydogen bonding in the O-ether complexes and (2) steric hindrance associated with the $O\text{-}CH_3$ group. Since the lack of hydrogen bonding, as such, would not be expected to lead to an abnormal stability order, steric hindrance may be the more important of the two effects. The greatly lowered stability of the nickel complex as compared with that of the nickel dimethylglyoxime chelate, however, suggests that the lack of hydrogen bonding may be an important factor here. It is also possible that the steric interference between reagent molecules in the formed complex MR_2 may prevent a coplanar arrangement about the nickel atom leading to lower stability. The same effect may account for the apparent difficulty in introducing a second chelate anion about a copper ion. It is noteworthy, while considering steric hindrance, that there was no evidence of complex formation between the O-ether and Pb (II), the largest atom used, under the conditions employed. It is possible that the presence of the O-CH_3 group in the reagent may interfere with the approach of the large lead ion. The fact that the stabilities of the Zn (II) and Cd (II) complexes of the O-ether appear to be greater than those of the corresponding dimethylglyoxime chelates is difficult to explain. It can be said, however, that the complexes in these cases would be expected to be tetrahedral. In such cases steric hindrance between reagent molecules in the formed complex might not be so important as with the planar complexes. It should be mentioned that differences in stability between the complexes of dimethylglyoxime and its O-ether cannot be attributed to differences in acid dissociation constants, since, as mentioned above, the values of K_{OH} are nearly the same for the two reagents.



where R = H or CH_3

An additional factor not considered above, is the fact that the type of bonding within the chelates of dimethylglyoxime and of its O-ether has, in most cases, not been established. The nickel atom in the nickel chelate of dimethylglyoxime is known to be bound to the four oxime nitrogen atoms of the reagent molecules[5]. As pointed out above, it appears likely from the very similar formation curves obtained for the nickel, copper, and cobalt complexes, together with other evidence, that these are similarly constituted. It is conceivable, however, that the chelates of dimethylglyoxime and its O-ether with some of the other metals may involve linkage through an oxime oxygen atom, to give six-membered rings, as shown in the attached formula.

Such a case, while not affecting the calculation of constants, would almost certainly have an effect on the stability of the chelates involved. Further discussion of this point must await additional structural studies.

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SUMMARY

The titration procedure described in previous papers of this series has been applied to a study of some metallic chelates of dimethylglyoxime and of its O-monomethyl ether. Evidence is presented for the existence of dimethylglyoxime chelates with Zn (II), Pb (II), Cd (II), and La (III) in addition to the known Cu (II), Ni (II), and Co (II) complexes. Formation constants are calculated for these complexes, and for those of dimethylglyoxime O-monomethyl ether, on the basis of their most probable structures. The results indicate that the famed specificity of dimethylglyoxime for nickel does not lie in any special stability of this chelate, but in some other factor, possibly solubility. A comparison of the chelates of dimethylglyoxime with those of its O-ether is discussed in terms of such structural factors as hydrogen bonding and steric hindrance. Heat content and entropy changes have been calculated for the chelation of dimethylglyoxime with Cu (II) and Ni (II) ions.

RÉSUMÉ

La méthode titrimétrique, décrite dans des publications précédentes, a été appliquée à l'étude de quelques complexes métalliques de la diméthylglyoxime et de son éther O-monométhylique. On a pu prouver l'existence de complexes de la diméthylglyoxime avec Zn (II), Pb (II), Cd (II) et La (III), en plus de ceux déjà connus de Cu (II), Ni (II) et Co (II). Les constantes de formation de ces complexes, ainsi que celles de l'ester O-monométhylique, ont pu être calculées, d'après leurs structures les plus probables. La spécificité bien connue de la diméthylglyoxime pour le nickel n'est pas due à une stabilité spéciale, mais à d'autres facteurs tels que la solubilité. On a fait également une étude comparative des complexes de la diméthylglyoxime et de ceux de son O-éther du point de vue de leur structure: liaison hydrogène et empêchement stérique. Et on a calculé la chaleur interne et la variation de l'entropie lors de la formation des complexes de la diméthylglyoxime avec le cuivre (II) et le nickel (II).

ZUSAMMENFASSUNG

Die vorherbeschriebene Titrierungsmethode ist zur Untersuchung gewisser Metalkomplexe von Dimethylglyoximen und deren O-Monomethyläther angewandt worden. Die Existenz der Dimethylglyoximkomplexe von Zn (II), Pb (II), Cd (II), und La (III), ausser der vorherbekannten Komplexen von Cu (II), Ni (II), und Co (II) ist nachgewiesen worden. Die Bildungskonstanten für diese Komplexe sowie die der Dimethylglyoxim-monomethyläther wurden auf Grunde der wahrscheinlichsten Strukturen berechnet. Die Ergebnisse zeigen, dass die bekannte Spezifizität des Dimethylglyoxims für Nickel nicht in der grösseren Beständigkeit dieses Komplexes, sondern in einer anderen Ursache, möglicherweise der Löslichkeit zu suchen ist. Die Komplexe des Dimethylglyoxims und dessen O-Äther sind verglichen worden auf Grund struktureller Eigenschaften wie Wasserstoffbrücken und sterischer Hinderung. Die Wärmetönung und die Entropie der Komplexbildung des Dimethylglyoxims mit Cu (II) und Ni (II) wurden berechnet.

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LA RÉACTION MERCURE(II)—*p*-DIMÉTHYLAMINOBENZALRHODANINE ET LA DÉTERMINATION DE MICROQUANTITÉS DE CYANURE*

par

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STRAFFORD ET WYATT[1] ont recommandé la réaction colorée de l'ion mercurique avec la *p*-diméthylaminobenzalrhodanine pour le dosage photométrique de petites quantités de mercure. OHLWEILER[2,3], se basant sur l'action complexante de l'ion cyanhydrique vis-à-vis de l'ion mercurique, a appliqué cette réaction à la détermination de microquantités de cyanure. La méthode consiste essentiellement à traiter la solution contenant le cyanure par un excès bien déterminé de nitrate mercurique, à ajuster convenablement l'acidité du milieu et à additionner le réactif organique sous forme d'une solution alcoolique à 0.02%. Le cyanure complexe une quantité approximativement équivalente de mercure, avec formation de cyanure mercurique non ionisé, et seulement l'excès non complexé est alors capable de réagir avec la *p*-diméthylaminobenzalrhodanine.

La *p*-diméthylaminobenzalrhodanine réagit sur l'ion mercurique, donnant un produit coloré très peu soluble. Quand la concentration du mercure est faible (par exemple, jusqu'à 2 p.p.m.), il se forme une dispersion très finement divisée et relativement stable. La nature colloïdale du système coloré est responsable des désavantages que présente la *p*-diméthylaminobenzalrhodanine comme réactif pour la détermination photométrique du mercure. Ces désavantages sont les suivants: a) la réaction dépend de l'acidité du milieu, qui pour cela doit être rigoureusement contrôlée; b) la présence des sels affecte l'absorption et la reproductibilité du système; c) l'absorption de la dispersion du rhodanate mercurique dépend de la température.

Tous les désavantages ci-dessus apparaissent également dans la méthode originale d'OHLWEILER pour la détermination de microquantités de cyanure. Le présent travail permet d'éviter les difficultés occasionnées par les effets d'acidité et de la présence des sels étrangers moyennant l'application de la technique de microdiffusion de CONWAY. L'innovation proposée consiste à traiter la solution à analyser avec de l'acide tartrique dans le compartiment externe d'une capsule de CONWAY. L'acide cyanhydrique libéré diffuse et il est absorbé par une solution de nitrate mercurique de concentration parfaitement définie située dans la partie interne de la capsule. La séparation du cyanure par microdiffusion élimine la présence de sels étrangers. En plus de cela, il assure le facile contrôle d'acidité de la solution résultante. Finalement la microdiffusion du cyanure constitue un procédé élégant pour la séparation de cette substance, opération nécessaire en certains cas. La séparation par microdiffusion est plus simple que les procédés par distillation ou aération et, principalement, plus convenable pour les cas de microquantités. La microdiffusion élimine encore l'interférence d'halogénures, mais non celle du thiocyanate, en relation avec la réaction du mercure (II) avec la *p*-diméthylaminobenzalrhodanine. Quant à l'effet de la température, il fut vérifié que ses variations causent seulement un déplacement vertical des courbes d'étalonnage. La correction est facilitée par la détermination d'un point supplémentaire lors de l'analyse.

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* Sous l'auspice du Conselho Nacional de Pesquisas.

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Appareils et matériaux spéciaux. a) Colorimètre photoélectrique Klett-Summerson. Par manque de filtres plus convenables, nous avons utilisé celui de 420 mμ. Le filtre le plus recommandable est celui de 470 mμ.

b) Capsules de CONWAY. Nous avons utilisé des capsules avec les dimensions internes suivantes: diamètre de la capsule, 6.5 cm; hauteur de la capsule, 1.3 cm; diamètre du compartiment interne, 4.0 cm; hauteur du compartiment interne, 0.8 cm.

c) Lubrifiants. Dans les essais de microdiffusion du cyanure, effectués à la température du laboratoire, le lubrifiant employé fut un mélange d'une partie de vaseline et de deux parties de lanoline (p. f. = 40° C). Dans les essais à 38° C, il fut employé un mélange en parties égales de vaseline et paraffine (p. f. = 50° C).

Réactifs. a) *p*-Diméthylaminobenzalrhodanine. Peser 0.100 g du produit (Eastman Kodak Co.) et dissoudre dans 500 ml d'alcool éthylique. Laisser au repos pendant la nuit et filtrer.

b) Acide nitrique 1*N*. Mesurer 200 ml du réactif concentré, additionner 50 ml d'eau et faire bouillir afin d'éliminer l'acide nitreux. Déterminer la normalité de la solution résultante et préparer, par dilution, la solution d'acide nitrique 1*N*.

c) Acide nitrique 0.005*N*. Préparer, moyennant dilution, à partir de la solution d'acide nitrique 1*N*.

d) Solutions de nitrate mercurique. Peser 0.500 g de mercure pur et dissoudre dans 5 ml d'acide nitrique. Additionner 10 ml d'eau, faire bouillir pour éliminer les oxydes d'azote, délayer avec 250 ml d'eau et faire bouillir de nouveau. Finalement, délayer la solution résultante à 1 litre; 1 ml de la solution contiendra 0.500 mg de mercure. A partir de la solution citée, moyennant dilution de volumes adéquats en acide nitrique 0.005*N* (pour empêcher l'hydrolyse du sel mercurique), préparer des solutions contenant 5, 10 et 12.5 γ de mercure par ml.

e) Solutions de cyanure de potassium. Préparer une solution approximativement 0.1*M* moyennant dissolution d'environ 6.5 g de cyanure de potassium dans 1 litre d'eau. Déterminer la concentration de la solution au moyen d'un titrage avec le

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nitrate d'argent selon la méthode de Dénigès. Au moment de l'usage, préparer, par dilution, les solutions plus diluées.

f) Solution saturée d'acide tartrique. Peser approximativement 100 g d'acide tartrique et saturer avec 100 ml d'eau.

ÉTUDE CRITIQUE DE LA RÉACTION MERCURE (II)-*p*-DIMÉTHYLAMINOBENZALRHODANINE

La partie expérimentale du présent travail commence par l'étude critique des facteurs qui influent dans les caractéristiques du système coloré formé par dispersion du rhodanate mercurique. Parmi ces facteurs, on compte l'acidité de la solution finale, l'excès du réactif, la température, la technique d'addition du réactif, la présence de sels étrangers et l'exposition à la lumière.

Effet de l'acidité. La coloration peut être développée en solution neutre ou acétique, mais alors elle serait largement masquée par la coloration jaune due à l'excès du réactif. L'acidification soignée avec de l'acide nitrique permet d'éliminer presque totalement la coloration de l'excès de la *p*-diméthylaminobenzalrhodanine, sans porter préjudice à la réaction du mercure avec le réactif organique. L'acidité ne doit pas être excessivement élevée parce qu'alors la formation de la substance colorée serait partiellement ou même totalement empêchée.

Dans le procédé de STRAFFORD ET WYATT, le réactif est utilisé sous forme d'une solution alcoolique à 0.02%. Il est additionné dans la proportion de 3 ml pour 100 ml de solution finale. Les auteurs cités recommandent de développer la coloration en présence d'acide nitrique 0.05*N*.

Après les observations faites sur le comportement du réactif, en partie déjà signalé par CAVE ET HUME[4], dans une récente étude sur la réaction de l'argent avec la *p*-diméthylaminobenzalrhodanine, nous avons modifié les conditions d'acidité. Par exemple, nous avons vérifié qu'en additionnant le réactif dans la proportion de 3 ml pour 100 ml de solution finale, contenant de l'acide nitrique 0.05*N*, la *p*-diméthylaminobenzalrhodanine présente une tendance à la floculation plus ou moins rapide selon la température. Tout se passe comme si la rhodanine formait une solution sursaturée dans laquelle apparaitrait lentement un précipité de rhodanine. L'élévation de la température diminue la vitesse de floculation, mais même à 28° C, la floculation se produit tout de suite après l'addition du réactif. L'augmentation de l'acidité du milieu permet également de retarder la floculation. Une acidité égale à 0.08*N* est capable d'empêcher la floculation de la rhodanine au moins pendant 20 minutes, même à la température de 11° C.

L'effet de l'acidité doit être encore considéré en fonction de l'absorption et de la stabilité de la dispersion du rhodanate mercurique. Pour cela, 97 ml des solutions ayant des concentrations variables d'acide nitrique et contenant approximativement 1 p.p.m. de mercure furent traités par 3 ml de solution alcoolique du réactif. Les absorptions trouvées sont représentées graphiquement dans la Fig. 1, courbe I. On voit que, pour les concentrations d'acide nitrique supérieures à 0.065*N*, l'absorption diminue graduellement. Cependant, l'utilisation d'une acidité correspondant à l'acide nitrique 0.08*N* est parfaitement admissible si les variations de l'acidité autour de la valeur mentionnée ne dépassent pas plus de 2%.

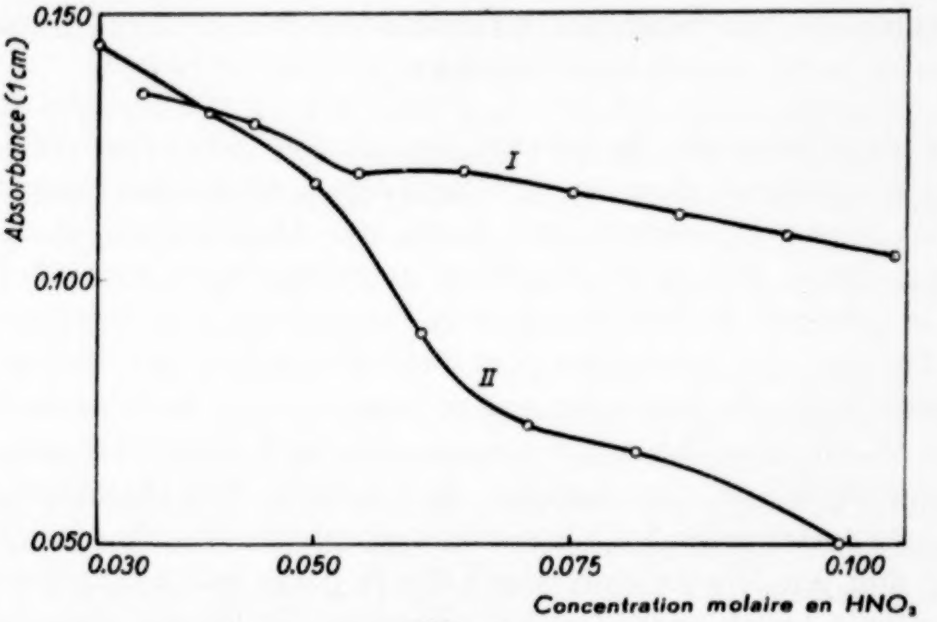

Fig. 1

Effet de l'excès du réactif. En traitant des solutions contenant la même concentration de mercure avec des volumes divers de la solution alcoolique de *p*-diméthylaminobenzalrhodanine, on observe que l'absorption du système est très sensible à l'excès du réactif. Dans la Fig. 2, les courbes I et II furent obtenues moyennant l'addition de 3 et 4 ml, respectivement, du réactif à des solutions avec concentrations diverses de mercure, d'un volume final de 100 ml et ayant une acidité égale à 0.08*N*; les courbes furent obtenues à la température de 31° C.

Les courbes sont approximativement linéaires, seulement dans leur partie initiale. La partie approximativement linéaire augmente avec l'excès du réactif. On peut en dire de même des valeurs de l'absorption. Nous avons maintenu le volume de 3 ml comme limite pratique imposée par la tendance à la floculation du réactif dans les essais à blanc ou de ceux contenant peu de mercure. Il est vrai qu'on pourrait diminuer la tendance de floculation. Ainsi, même à 13° C, on n'observe pas de floculation, jusqu'à 20 minutes, quand on additionne 4 ml du réactif à une solution mesurant finalement 100 ml, d'acidité égale à 0.06*N* et contenant 0.2% de gélatine. Comme la gélatine contient généralement du chlorure, elle n'a pas été utilisée. La présence d'acétone, comme l'ont observé déjà CAVE ET HUME, dans le travail antérieurement cité, diminue aussi la vitesse de floculation de la *p*-diméthylaminobenzalrhodanine. Mais, alors l'absorption du système est largement affectée par les variations d'acidité. Le fait est illustré par la courbe II de la Fig. 1, qui correspond à des solutions contenant approximativement

1 p.p.m. de mercure et 6% d'acétone et ayant une acidité égale à 0.06N, traitées avec 3 ml du réactif.

Effet de la température. La température est un autre facteur qui influe dans les caractéristiques d'absorption de la dispersion du rhodanate mercurique. Les courbes I et III de la Fig. 2 correspondent à des solutions de caractéristiques égales avec la seule différence que la courbe I fut obtenue à 31° C et la courbe III à 20° C. Les courbes données attestent une variation d'absorption approximativement de 0.003 unités pour une différence de 11° C. De plus, on voit que les variations de température causent un déplacement vertical de la courbe.

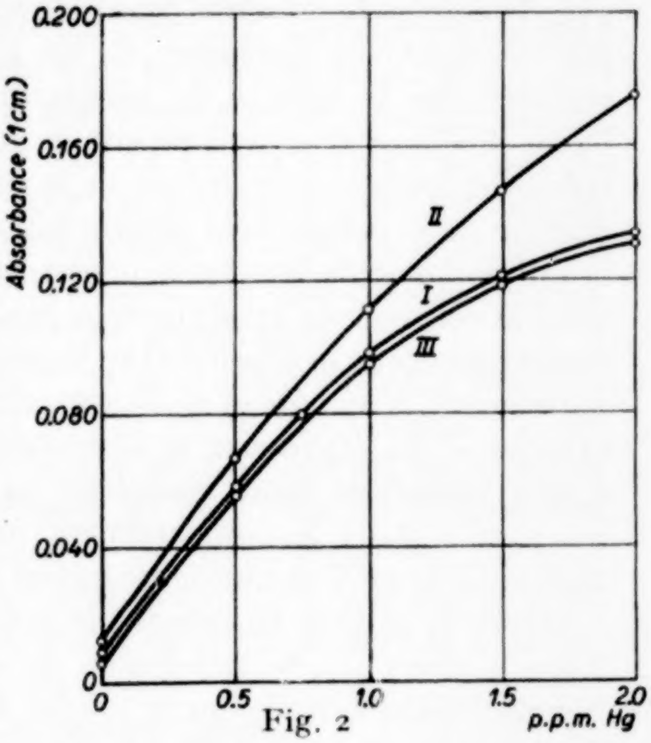

Fig. 2

Effet de la technique d'addition du réactif et du temps. La manière d'additionner la solution alcoolique de la rhodanine et le temps passé après l'addition ont un effet sensible sur l'absorption de la suspension résultante. STRAFFORD ET WYATT conseillent la simple addition du réactif à la solution suivie d'agitation. CAVE ET HUME, dans leur étude sur la réaction argent-*p*-diméthylaminobenzalrhodanine, recommandent d'additionner le réactif, lentement, avec une microburette, en même temps que la solution est agitée. Cette technique n'a pas permis l'obtention de données reproductibles dans le cas du mercure. De plus, le rhodanate mercurique obtenu dans ces conditions présente la tendance à la floculation. Des résultats reproductibles furent obtenus par addition du réactif à l'aide d'une pipette et agitation de la solution. Ainsi, des essais successifs, qui ont consisté à additionner d'après la forme indiquée, 3 ml du réactif à 97 ml d'une solution contenant approximativement 1.5 p.p.m. de mercure et ayant une acidité égale à 0.08N, ont présenté, après 20 minutes, les absorptions suivantes: 0.114, 0.114, 0.115, 0.115, 0.115, 0.114 et 0.115.

Les données de la Table I montrent l'effet du temps en relation avec le développement de la coloration; les valeurs de l'absorption correspondent à l'addition de 3 ml du réactif à 97 ml de solutions contenant des concentrations diverses de mercure et toutes de concentration 0.08N en relation avec l'acide nitrique. Quand la concentration du mercure est très faible, par exemple, 0.1 p.p.m., l'absorption augmente au début, atteignant un maximum entre 15 et 20 minutes et, après, elle diminue. Dans les cas de concentrations plus grandes (au-dessus de 0.5 p.p.m.), elle diminue graduellement. Devant ce fait, il faut arbitrairement établir un certain temps pour la mesure de l'absorption, par exemple, 20 minutes.

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DÉTERMINATION DU CYANURE

Procédé recommandé. Diluer la solution à un volume bien défini, de manière qu'elle contienne jusqu'à 3 γ de CN^- par ml. Transvaser avec une pipette de 2.500 ± 0.005 ml de la solution résultante dans le compartiment externe d'une capsule de CONWAY. Transvaser dans le compartiment interne 2.500 ± 0.005 ml de solution de nitrate mercurique contenant 12.5 γ de Hg^{+2} par ml. Fermer la capsule avec le couvercle de verre émeri dûment lubrifié. Incliner la capsule légèrement, par exemple, en reposant un de ses bords inférieurs sur un couvercle, de manière que le liquide du compartiment externe reste dans la partie la plus basse. Prélever avec une pipette 1 ml de la solution saturée d'acide tartrique, retirer légèrement le couvercle de la capsule, suffisamment pour permettre l'introduction de la pointe de la pipette dans le compartiment externe et laisser s'écouler la solution d'acide tartrique, autant que possible, en évitant qu'elle ne se mélange avec la solution de cyanure déjà placée dans le compartiment externe. Fermer hermétiquement la capsule avec le couvercle. Incliner la capsule, avec soin, alternativement, d'un côté et de l'autre, afin de mélanger les réactifs du compartiment externe et de provoquer la libération d'acide cyanhydrique. Laisser pendant le temps nécessaire pour compléter la diffusion de l'acide cyanhydrique et son absorption dans le compartiment interne (deux heures pour une température ambiante de 27° C et une heure quand la diffusion est faite dans une étuve à 38° C).

Ouvrir la capsule en retirant le couvercle de verre. Prélever avec une pipette 2.000 ± 0.005 ml de la solution du compartiment interne et laisser s'écouler le liquide dans un erlenmeyer de 200 ml. Ajouter 42.5 ± 0.1 ml d'eau exempte de chlorure et 4.00 ± 0.01 ml d'acide nitrique 1.00 ± 0.02*N*. Agiter l'erlenmeyer pour homogénéiser parfaitement la solution résultante. Laisser s'écouler d'une pipette 1.500 ± 0.005 ml d'une solution alcoolique de *p*-diméthylaminobenzalrhodanine à 0.02%, dans l'erlenmeyer, en agitant en même temps la solution. Laisser la solution pendant 20 minutes en un lieu obscur. Mesurer l'absorption à 480 mμ ou avec l'aide d'un filtre adéquat, l'appareil étant réglé avec de l'eau pour une transmission de 100%.

Courbe étalon. La Fig. 3 montre une courbe étalon capable de permettre la détermination jusqu'à 6 γ de CN^- (ou, plus exactement, 3 γ de CN^- par ml de la solution originale). Des courbes similaires peuvent être préparées avec 2.000 ± 0.005 ml de solutions contenant des quantités connues de cyanure (par exemple, 0, 1.25,

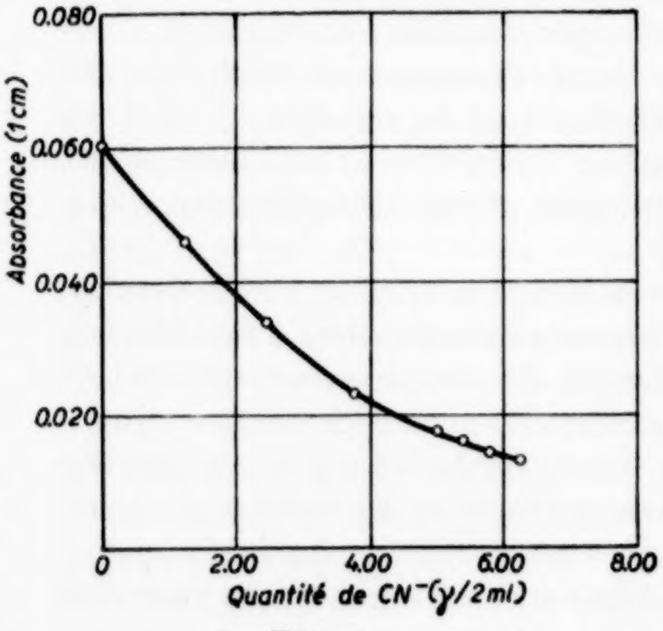

Fig. 3

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2.50, 4.00, 5.00, 5.50 et 6.00 γ de CN^-) et 2.000 ± 0.005 ml d'une solution de nitrate mercurique contenant 12.5 γ de Hg^{+2} par ml. Les solutions sont transvasées dans un erlenmeyer de 200 ml, diluées avec 40.5 ± 0.1 ml d'eau exempte de chlorure et traitées avec 4.00 ± 0.01 ml d'acide nitrique 1.00 ± 0.02*N*. Après avoir agité la solution résultante, le développement de la coloration et la mesure de l'absorption sont faites comme dans le procédé recommandé.

En ce qui concerne l'effet de la température sur l'absorption des dispersions du rhodanate mercurique, la température doit être contrôlée à 2° C à peu près, ou alors, la courbe doit être construite simultanément avec la détermination du cyanure. Comme les variations de température causent simplement un déplacement vertical de la courbe (0.003 unités pour une différence de 11° C) une manière de corriger pratiquement l'effet de la température est celle qui consiste à effectuer, parallèlement à l'analyse, un essai avec une solution exempte de cyanure. Le déplacement de l'absorption correspondant au point zéro de l'échelle des quantités de cyanure, sera suffisant pour faire la correction de l'effet de température.

Données expérimentales. Le temps nécessaire pour la microdiffusion complète du cyanure fut trouvé expérimentalement au moyen de deux séries d'essais avec 2.5 ml d'une solution contenant près de 3 γ de CN^- par ml. La quantité de cyanure prise correspond approximativement au maximum de cyanure qui peut être déterminé par le procédé recommandé. Les deux séries d'essais sont différentes uniquement en ce qui concerne la température. Dans la première série, la diffusion fut effectuée à la température ambiante de 27° C et, dans la seconde, les capsules furent laissées dans une étuve chauffée à 38° C. Dans chacune des séries, on a fait varier le temps donné pour la microdiffusion.

Les résultats trouvés sont donnés dans le Tableau I.

TABLEAU I

TEMPS NÉCESSAIRE POUR LA MICRODIFFUSION

Température (° C)	Temps	Absorbance (1 cm)
27	1 h	0.024
	2 h	0.018
	3 h	0.018
38	30 min	0.021
	1 h	0.018
	1 h 30 min	0.018

Par conséquent, l'élévation de la température de 27 à 38° C réduit pratiquement à la moitié le temps nécessaire pour la complète microdiffusion. Des essais parallèles, dans les mêmes conditions, excepté en ce qui concerne la microdiffusion laquelle fut omise et substituée par l'addition directe du cyanure à la solution contenant le mercure, ont conduit également à l'absorbance de 0.018, montrant le sens quantitatif de la microdiffusion et la possibilité de préparer des courbes étalon directement.

Afin de vérifier la précision de la méthode, deux séries d'essais furent réalisées respectivement, avec des solutions de cyanure contenant 0.60 et 2.70 γ de CN^- par ml. Les résultats trouvés sont ceux du Tableau II.

TABLEAU II

ESSAIS POUR LA CARACTÉRISATION DE LA PRÉCISION

Quantité de cyanure (γ/2 ml)	Essai	Absorbance (1 cm)
1.20	1	0.045
	2	0.046
	3	0.046
	4	0.046
	5	0.046
	6	0.045
	7	0.046
		Écart normal: 0.0005
5.40	1	0.016
	2	0.016
	3	0.016
	4	0.016
	5	0.015
	6	0.016
	7	0.015
		Écart normal: 0.0005

La précision de la méthode, donnée par l'écart normal, en coefficient d'extinction, est égale à 0.0005. Ayant en vue le caractère non rectiligne de la courbe étalon, l'inclinaison de celle-ci varie et, par conséquent, aussi l'effet de l'imprécision au long de l'échelle des quantités de cyanure qu'on peut déterminer. Dans la partie initiale de la courbe (0 jusqu'à 2 γ), une différence d'absorption égale à 0.0005 correspond à près de 0.02 γ de CN^-, tandis que, dans la partie finale (4 à 6 γ) elle représente 0.05 γ de CN^-.

RÉSUMÉ

Les auteurs ont réalisé initialement une étude critique des divers facteurs qui affectent la réaction du mercure (II) avec la *p*-diméthylaminobenzalrhodanine. La deuxième partie du travail représente une révision de la méthode de détermination du cyanure, antérieurement proposée par OHLWEILER,[2,3] basée sur l'action complexante de l'ion cyanhydrique sur l'ion mercurique et dans la réaction colorée de ce dernier avec le réactif organique cité. Pour tourner les difficultés provenant de la nécessité de fixer rigoureusement l'acidité et de l'action gênante de sels étrangers, il est recommandé de séparer préalablement le cyanure par microdiffusion et de l'absorber dans une solution de nitrate mercurique selon la technique de CONWAY.

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Le procédé recommandé permet de déterminer jusqu'à 6 γ de CN^-. Cette quantité diffuse quantitativement en 2 heures à la température de 27° C ou en 1 heure à l'étuve à 38° C. L'écart normal varie de 0.02 à 0.05 γ de CN^- le long de l'échelle des quantités déterminables de cyanure.

SUMMARY

The paper opens with a critical study of several factors affecting the reaction of mercury (II) with *p*-dimethylaminobenzalrhodanine. The second part of the paper reviews the method of cyanide determination formerly recommended by OHLWEILER[2,3] based on the mashing action of cyanide ion on the color reaction of the mercuric ion with the organic reagent mentioned above. In order to avoid difficulties in keeping acidity strictly adjusted and the interference of foreigns salts, this article suggests the previous separation of the cyanide by microdiffusion and its absorption in a mercuric nitrate solution, following CONWAY's technique. Quantitative diffusion of CN^- up to 6 γ takes place in one hour at room temperature of approximately 27° C and in one hour at 38° C, when inside an electric oven. Recommended procedure allows the determination up to 6 γ. The standard deviation ranges from 0.02 to 0.05 γ of CN^- along the scale of the determinable cyanide quantities.

ZUSAMMENFASSUNG

Die Verfasser führten im ersten Teil eine prüfende Untersuchung der verschiedenen Faktoren, welche die Reaktion des Quecksilbers (II) mit *p*-Dimethylaminobenzalrhodanin beeinflussen, aus. Der zweite Teil der Arbeit besteht in einer Neuuntersuchung der vom erstgenannten Verfasser früher vorgeschlagenen Zyanidbestimmungsmethode, die auf der Komplexierung des Merkuriions durch Zyanidion, und der Farbreaktion des ersteren mit dem erwähnten organischen Reagens, beruht. Zur Umgehung der Schwierigkeiten, die sich aus der Notwendigkeit den Säuregehalt genau anzupassen, und aus der Interferenz fremder Salze ergeben, empfiehlt man die vorherige Abtrennung des Zyanids durch Mikrodiffusion und seine Aufnahme in Mercurinitratlösung, gemäss der Technik von CONWAY. Mengen bis zu 6 γ CN^- diffundieren quantitativ in 2 Stunden bei Raumtemperatur von 27° C, oder in 1 Stunde im Ofen bei 38° C. Das vorgeschlagene Verfahren ermöglicht bis zu 6 γ CN^- zu bestimmen. Die Normalabweichung schwangt zwischen 0.02 un 0.05 γ CN^- entlang der Skala der bestimmbaren Zyanidmengen.

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THE DETERMINATION OF POTASSIUM AND SODIUM IN COAL ASH

by

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Potassium and sodium in coal ash are generally determined by the classical method of LAWRENCE SMITH. After the mixed chlorides of potassium and sodium have been isolated, potassium is determined by the perchlorate or chloroplatinate method and sodium by difference. In their work on the analysis of silicates and of refractories, MILLER AND TRAVES[1] and HASLAM AND BEELEY[2] showed that the cumbersome separations involved could be eliminated by determining potassium and sodium directly on suitable aliquots of the leachings. Potassium was separated as the cobaltinitrite and converted to the perchlorate, in which form it was finally weighed; sodium was determined gravimetrically as sodium zinc uranyl acetate. These methods appeared to be suitable for application to the analysis of coal ash, but further work based on the following considerations was necessary:

1. MILLER AND TRAVES (*loc. cit.*) reported that calcium caused positive errors in the sodium determination, unless a reprecipitation was carried out. HASLAM AND BEELEY (*loc. cit.*), however, made no reference to this interference, but the position was further complicated by other workers[3] who claimed that calcium caused negative errors.
2. DUVAL[4] showed from thermogravimetric studies that sodium zinc uranyl acetate was not a satisfactory weighing form, as loss of water of crystallisation could occur at the drying temperature used. He recommended instead ignition between 360° and 674° C to the stable double pyrouranate, $\frac{1}{2}Na_2U_2O_7.ZnU_2O_7$.
3. The method for the determination of potassium was not convenient because of the lengthy procedure involved. HASLAM AND BEELEY (*loc. cit.*) weighed the cobaltinitrite precipitate without further treatment when potassium was present in very small amounts, but in all other cases the precipitate owing to its variable composition had to be converted to the perchlorate.

Other matters which appeared to be worthy of further examination were (a) the possibility of applying the flame photometer in the final determination of sodium and potassium and (b) the recent claim by LOGIE AND RAYNER[5] that a temperature of 1000° C is necessary for the complete decomposition of certain ashes.

DISCUSSION

BELCHER AND NUTTEN[6] suggested that, if the possible errors associated with the determination of sodium were significant, they could readily be eliminated — apart from the negative errors — by titration of the precipitate. Accordingly, they made a study of the alkalimetric titration of sodium zinc uranyl acetate, and as a result they developed a reliable titrimetric method for the determination of sodium. In the course of this work it was shown that calcium in amounts likely to be present after ignition by the LAWRENCE SMITH method had no effect on the gravimetric determination of sodium. Any variation in the water of crystallisation appeared to be too slight to affect the results significantly. There was little to choose between the gravimetric and alkalimetric finishes as regards either speed or accuracy.

At the outset of this work (some 7 years ago) the 32 methods then available for the determination of potassium involving the precipitation of a sparingly soluble compound were considered. These methods could be divided into two categories.

(a) those which had been subjected to extensive examination, and about which considerable information was available and (b) those which had received little or no attention since being advanced.

In the first group only the cobaltinitrite method appeared to be worthy of further examination. The method had the advantage of being selective and rapid. Although the composition of the precipitate was known to vary, conditions had been described by several workers which were claimed to yield a precipitate of stoichiometric composition.

In the second group, precipitation as the phosphomolybdate appeared to be the most attractive method as it combined the advantages of selectivity and rapidity with stoichiometry.

Both the cobaltinitrite and phosphomolybdate methods have since been investigated, and, after suitable modifications, fairly satisfactory procedures have been developed for the determination of potassium. Thus, BELCHER AND NUTTEN[7] examined several modifications of the cobaltinitrite method which had been claimed to yield precipitates of stoichiometric composition, but they could not confirm these claims. They did, however, obtain a precipitate of fairly constant composition by following the procedures of DRUSHEL and of HAMID[8] which appeared to be identical, but they had to apply an empirical factor to obtain the true amount of potassium present. The method was somewhat less accurate than the perchlorate method.

An X-ray and electron microscopic examination of cobaltinitrite precipitates[9] revealed that owing to mixed crystal formation a precipitate of stoichiometric composition could only be obtained by chance. With regard to the precipitation of potassium as the phosphomolybdate, BELCHER AND ROBINSON[10] found that

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the fine state of subdivision of the precipitate entailed special care in filtering and that the precipitate was more soluble than any of the cobaltinitrite precipitates.

Although there were detractions to the cobaltinitrite and phosphomolybdate methods, no other procedures were available at that time possessing all the desired features. Since then, however, WITTIG and his co-workers[11] have determined potassium rapidly, selectively and accurately as the sparingly soluble potassium tetraphenylboron using sodium tetraphenylboron as reagent. KOHLER[12] has applied the method to potassium solutions containing mineral acid, whilst other workers[13] have proposed various procedures for the titrimetric determination of the precipitate. A review of the literature concerning this reagent has recently been compiled by NUTTEN[14].

We have substantiated under a variety of conditions the claims which have been made regarding the determination of potassium as potassium tetraphenylboron. There is no doubt that this method will rank as one of the most important contributions ever made to analytical chemistry, because for, the first time, potassium can be determined selectively, rapidly and accurately, and moreover, the precipitate is of stoichiometric composition. The high equivalent weight of the complex and the resulting low conversion factor (0.13143) are unusually favourable.

With the above considerations in mind we carried out a comprehensive and critical examination of the application to coal ash of various methods for the determination of sodium and potassium. Three samples of coal ash and a standard glass* were used in the investigation.

EXAMINATION OF RESULTS

Sodium and potassium were determined in triplicate by the method described in Fuel Research Survey Paper No. 50 (D.S.I.R.), except that after weighing the mixed chlorides, sodium was determined gravimetrically by the triple acetate method and potassium was obtained by difference. The results are included in Table I.

TABLE I

DETERMINATION OF POTASSIUM AND SODIUM BY THE LAWRENCE SMITH METHOD

	K_2O%	Na_2O%
Standard Glass No. 1 (K_2O = 0.80%, Na_2O = 13.25%)	0.80	13.28
Coal Ash A	2.62	0.86
Coal Ash B	3.01	0.54
Coal Ash C	1.25	1.15

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* Soc. Glass Tech. Standard Glass No. 1, *J. Soc. Glass Tech.*, 34 (1950) 258.

Determination of sodium

A comparison of results obtained by the triple salt methods (gravimetric and titrimetric) and using a flame photometric technique is given in Table II. After ignition by the LAWRENCE SMITH method, the sodium was determined directly on a suitable aliquot of the aqueous extract. The instrument used for the flame photometric work was the "EEL" flame photometer (Evans Electroselenium Ltd., Essex). Calibration curves were prepared from "Specpure" sodium chloride (Johnson, Matthey, Ltd., London). Calcium (from "AnalaR" calcium carbonate) was added to the standards in amounts equal to those present in an actual determination (*ca.* 0.2 g per 100 ml), allowance being made for the sodium content of the calcium carbonate.

TABLE II

DETERMINATION OF SODIUM BY VARIOUS METHODS (LAWRENCE SMITH IGNITION)

	Temp. of decomposition °C	Na_2O% Gravimetric	Titrimetric	Flame Photometer
Standard Glass No. 1	1000	13.25	13.28	13.07
	,,	13.32	13.28	13.20
	,,	13.30	—	—
Coal Ash A	800	0.83	0.86	—
	1000	0.85	0.86	—
	,,	0.88	0.87	0.90
	,,	0.82	0.84	0.84
Coal Ash B	800	0.53	0.51	—
	,,	0.49	0.48	—
	1000	0.56	—	0.59
	,,	0.54	0.52	—
Coal Ash C	800	1.10	1.09	—
	1000	1.14	1.13	1.17

The calibration curves covered the range 0-6 p.p.m. Na_2O. Aliquots of the sample solutions were diluted so that the sodium content came within this range.

It will be seen from Table II that the results obtained using the flame photometer were somewhat less reproducible than those obtained using either of the triple acetate methods, but they are satisfactory for most purposes. As the apparatus is not generally available, the method will not be described in further detail, but it is mentioned as a rapid alternative procedure for the determination of sodium (and of potassium). The findings of LOGIE AND RAYNER[5] that no loss of alkali occurred when the ignition was effected at 1000° C were confirmed. Indeed, when ignition was done at this temperature our results tended to be slightly higher than when the ignition was done at 800° C.

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Determination of potassium

Potassium was determined on suitable aliquots of the extract after ignition by the LAWRENCE SMITH procedure or decomposition by the BERZELIUS method. The results using the gravimetric perchlorate, cobaltinitrite and tetraphenylboron methods and the titrimetric phosphomolybdate method are listed in Table III.

TABLE III

DETERMINATION OF POTASSIUM BY VARIOUS METHODS

	Method and temp. (° C) of decomposition	Perchlorate	Cobaltinitrite	Tetraphenylboron	Phosphomolybdate	Flame photometer
Standard Glass No. 1	L.S. 1000	—	0.83	0.79	0.79	—
	,, ,,	—	—	0.80	0.75	0.79
	,, ,,	—	0.78	0.79	0.79	—
Coal Ash A	,, 800	—	2.63	—	—	—
	,, 1000	—	2.64	2.61	2.60	2.54
	,, ,,	2.60	—	2.61	2.63	2.62
	,, ,,	—	2.54	2.63	2.67	2.60
	Berzelius	2.62	—	2.60	—	2.60
Coal Ash B	L.S. 800	—	2.96	2.96	—	—
	,, 1000	—	3.14	3.04	3.05	—
	,, ,,	—	3.03	3.04	3.02	3.02
	,, ,,	3.00	—	2.97	—	3.00
	Berzelius	2.98	—	3.02	2.95	3.04
	,,	—	—	2.98	—	3.08
Coal Ash C	L.S. 1000	—	—	1.23	1.21	1.20

L.S. = Lawrence Smith.

Results using the flame photometer are included in the last column of the Table, and again these are satisfactory for most purposes. Calibration curves for the photometer were prepared from "Specpure" potassium chloride, calcium being added to the standards as before. For ashes decomposed by the Berzelius procedure, acid was added to the standards, and of course the calcium was omitted. The calibration curves covered the range 0-12 p.p.m. K_2O, and aliquots of the sample solutions were diluted so that the potassium content came within this range.

Precipitation as potassium tetraphenylboron was the most rapid of the chemical methods, and the results compared favourably with those obtained by the perchlorate method. The tetraphenylboron method is also superior to the perchlorate procedure in that direct precipitation is possible in the presence of the sulphate ion. In view of this and the other advantages discussed earlier, we recommend the tetraphenylboron method for the determination of potassium in coal ash and silicates in general. Again, no loss of potassium occurred on igniting at 1000° C and this temperature is recommended in a general procedure for the ignition.

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EXPERIMENTAL

Reagents

Calcium carbonate (AnalaR).

Ammonium chloride (AnalaR).

Zinc uranyl acetate solution. Prepare the following solutions: — (a) Zinc acetate (427 g), 30% acetic acid (46 ml), water (527 ml). (b) Uranyl acetate (145 g), 30% acetic acid (92 ml), water (748 ml).

Prepare the solutions separately, applying heat to effect solution. Mix the hot solutions, add 2 ml of 0.1*N* sodium chloride solution, allow to stand for 24 hours and filter.

Ethanol: 95% saturated with sodium zinc uranyl acetate.

Ether. Anhydrous.

Sodium hydroxide. 0.1*N*.

*Sodium tetraphenylboron.** 0.6% aqueous solution. Dissolve 1.5 g of sodium tetraphenylboron in 250 ml of water. Add 0.5-1 g of aluminium hydroxide, stir for 5 minutes and filter. Prepare fresh each week.

Potassium tetraphenylboron. Saturated aqueous solution. Shake 20-30 mg of potassium tetraphenylboron with 250 ml of water for 30 minutes. Add 0.5 g of aluminium hydroxide and filter. Prepare fresh each week. The potassium salt may be stored in a desiccator.

Indicators. (a) *Phenolphthalein:* 1% in 95% ethanol.
(b) *Bromothymol blue:* 1% in 95% ethanol.

Procedure

Lawrence Smith ignition. Grind 0.5 g of the ash with 4 g of calcium carbonate and 0.5 g of ammonium chloride in an agate mortar. Place the mixture in a 30 ml tall form platinum crucible lined with 0.2 g of calcium carbonate and cover with a further 0.5 g of calcium carbonate.

Place the crucible in a hole in an asbestos sheet so that about $^1/_3$ of the crucible protrudes. Place a small beaker of cold water on the lid of the crucible. Heat gently over a Bunsen flame so that ammonia is evolved but no white fumes of ammonium chloride are seen. Continue this gentle heating until no further ammonia fumes are evolved (test with hydrochloric acid). Remove the crucible lid and heat gently to remove any ammonium chloride that has sublimed on to it. Replace the lid and heat with the full heat of a Meker burner for 1 hour. Replace the water in the beaker periodically. Cool the crucible and transfer the cake to a porcelain basin with 30 ml of hot water. Digest near the boiling point for 30 minutes. Allow to settle and decant through a filter. Extract the residue with 2 × 25 ml portions of boiling water and wash the filter with small portions of water. Add

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* Obtainable under the Trade Name "Kalignost' from Heyl & Co., Chem.: Pharm. Fabrik, Berlin-Steglitz v. Hildesheim.

1 or 2 drops of concentrated hydrochloric acid to the filtrate and dilute the filtrate to 100 ml in a graduated flask. Test for complete decomposition of the ash by dissolving the residue in hydrochloric acid. No gritty residue should remain.

Determination of sodium

Take a suitable aliquot (25 ml) of the Lawrence Smith extract and evaporate to dryness. Dissolve the residue in 1 ml of water and add 10 ml of the zinc uranyl acetate reagent. Stir for 10 minutes and filter after 1 hour on a No. 4 sintered-glass crucible. Wash with 5 × 2 ml portions of the reagent, allowing the crucible to drain completely after each addition, and then wash with 5 × 2 ml portions of 95% ethanol saturated with the triple salt. Finally wash with 2 × 2 ml portions of ether. Draw air through the crucible for 5 minutes, allow to stand in the balance case for 30 minutes and weigh.

1 mg of sodium zinc uranyl acetate $\equiv$ 0.02015 mg Na_2O. Alternatively dissolve the precipitate in the minimum amount of water and titrate with 0.1N sodium hydroxide using 2 drops each of phenolphthalein and bromothymol blue as indicator. The endpoint is the first shade of pink which appears from the green background.

1 ml 0.1N NaOH $\equiv$ 0.35147 mg Na_2O.

Determination of potassium

Take a suitable aliquot (25 ml) of the Lawrence Smith extract and add 0.2 ml of concentrated hydrochloric acid. Add 10 ml of 0.6% sodium tetraphenylboron solution, stir and allow to stand for 10-15 minutes. Filter on a No. 4 sintered-glass crucible, wash with 5 × 3 ml portions of a saturated aqueous solution of potassium tetraphenylboron. Dry for 30 minutes at 120° C and weigh as $K[B(C_6H_5)_4]$.

1 mg $K[B(C_6H_5)_4] \equiv 0.1314$ mg K_2O.

Notes

1. The Lawrence Smith ignition used is essentially that described by WESTWOOD AND MAYER[15]. The special Lawrence Smith crucibles may be used provided that the heating arrangement allows the upper part of the crucible to remain cool (see, for example, LOGIE AND RAYNER[5]).
2. It is essential that a blank be carried out on the reagents used.
3. 10 ml of 0.6% sodium tetraphenylboron are sufficient to precipitate 5 mg of K_2O (*i.e.* 4% K_2O in the ash on a 25 ml aliquot). If the potassium content of the ash is unusually high, either a smaller aliquot must be taken or the amount of reagent increased. With two platinum crucibles it is possible to determine sodium and potassium in two samples in one day.

SUMMARY

Methods are described for the rapid determination of sodium and potassium in coal ash. The ash is decomposed by a Lawrence Smith ignition: sodium is determined as sodium zinc uranyl acetate (gravimetrically or titrimetrically) on an aliquot of the aqueous extract, and potassium is determined gravimetrically as potassium tetraphenylboron on a second aliquot.

Other methods for completing the determination were examined but were less satisfactory. The flame photometer method although less reproducible than other methods is extremely rapid and is probably accurate enough for routine purposes.

RÉSUMÉ

Des méthodes sont décrites pour le dosage rapide du sodium et du potassium dans les cendres de charbon. Les cendres sont désagrégées par ignition (procédé Lawrence Smith): le sodium est dosé sous forme d'acétate triple de zinc, uranyle et sodium (gravimétriquement ou volumétriquement) sur une partie aliquote de la solution aqueuse; le potassium est dosé gravimétriquement au moyen du tétraphénylbore sur une autre partie aliquote. D'autres méthodes ont été examinées, mais elles sont moins avantageuses. Le procédé au photomètre de flamme, bien que moins reproductible que d'autres méthodes, est extrêmement rapide; il est probablement suffisamment précis pour des analyses en série.

ZUSAMMENFASSUNG

Methoden zur raschen Bestimmung von Natrium und Kalium in Kohlenaschen werden beschrieben. Die Asche wird nach der Methode von Lawrence Smith zersetzt; in einem Teil des wässrigen Extraktes wird das Natrium als Natrium-Zink-Uranyl-Acetat gravimetrisch oder titrimetisch bestimmt, in einem anderen Teil wird das Kalium gravimetrisch als Kaliumtetraphenylbor bestimmt. Andere Methoden wurden untersucht, erwiesen sich aber als weniger befriedigend. Die flammenphotometrische Methode gibt zwar weniger gut reproduzierbare Resultate als andere Verfahren, ist aber besonders rasch; für Serienanalysen ist sie wahrscheinlich genügend genau.

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CHROMATOGRAPHIC DETECTION OF SCANDIUM*

by

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INTRODUCTION

To facilitate a search for scandium-bearing ores, paper chromatographic methods were investigated as offering a convenient and rapid technique for detecting small quantities of this element without requiring elaborate or specialized equipment.

Previously reported work on the chromatography of scandium describes the separation of this element from the rare earths and thorium by means of a tetrahydrosylvan (tetrahydro-2-methylfuran) solution containing nitric acid with alizarin used as the developer. Tetrahydrosylvan was recommended as the preferred solvent but mention was made that the separation could also be effected by using methyl acetate.

A comparison of the results obtained by using both tetrahydrosylvan and methyl acetate as solvents indicated that the latter was more suitable as well as more readily available. Consequently, methyl acetate was selected for further study.

APPARATUS AND REAGENTS

Methyl acetate, technical, distilled at 57.1° C
Nitric acid, specific gravity 1.42
Quinalizarin, saturated solution in 95% ethanol
Test solutions
Chromatographic paper, Whatman Nos. 1,4 and 3 MM in rolls of 1 inch width
Beakers, 10 ml
Test tubes. 4 × 45 cm

METHOD

Downward diffusion of the solution was used. A strip of paper 40 cm long

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Reference p. 131.

was trimmed at one end so that it would fit into a 10 ml beaker and folded about 3.5 cm from the end. The folded end of the strip was then inserted into the beaker which was suspended near the top of the test tube by a wire bent over the lip of the test tube. The test tube was stoppered to hinder evaporation.

Samples were converted into nitrate solutions and adjusted to a pH of 2 with nitric acid. A 0.01 ml droplet was pipetted onto the paper strip and allowed to dry at room temperature. The treated portion of the paper should be about 5 cm from the fold so that it is below the bottom of the beaker when suspended in the test tube.

The solvent, composed of 85 parts by volume of methyl acetate, 5 parts nitric acid and 10 parts water was then placed in the beaker and the test tube stoppered. Some solvent was kept at the bottom of the tube to maintain saturation.

When the solvent had travelled a distance of approximately 30 cm the paper strip was removed, dried at room temperature, sprayed with quinalizarin solution and suspended without drying in an ammonia atmosphere for 5 to 10 minutes after which it was air dried thoroughly.

When immediate observations were desired, the alkaline color of the dye was removed by neutralizing the ammonia by spraying with an ethanol solution 1*M* with respect to acetic acid. Otherwise, the evaporation of the ammonia gradually restores the yellow color of the quinalizarin after which measurements can be made.

RESULTS

Quinalizarin was selected as a developer because it reacts with fewer of the commonly encountered ions. The possibility of interference from other ions was determined by testing solutions of other ions for a color reaction with quinalizarin under the same conditions encountered in chromatography. The results of the tests with ions that produced color are given in Table I. Ions that did not show any color reaction are listed in Table II.

TABLE I

COLORS OBTAINED WITH DIFFERENT IONS USING QUINALIZARIN AS DEVELOPER

Ion	Color	Ion	Color
Cu^{+2}	pink	ZrO^{+2}	blue-violet
Ni^{+2}	salmon pink	Sc^{+3}	red-violet
Al^{+3}	salmon pink	Th^{+4}	blue-violet
Fe^{+3}	brown	WO_4^{-2}	pink
Cr^{+3}	lavender (no color for several hours)	TiO_3^{-2}	blue
UO_2^{+2}	bluish gray	Rare earths	blue

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TABLE II

IONS NOT GIVING ANY COLOR WITH QUINALIZARIN

NH_4^+	Ba^{+2}	Pb^{+2}	Ce^{+4}
Na^+	Ca^{+2}	Co^{+2}	Sn^{+4}
K^+	Sr^{+2}	Mn^{+2}	GeO^{+2}
Li^+	Cd^{+2}	Sn^{+2}	AsO_3^{-3}
Hg_2^{+2}	Zn^{+2}	Sb^{+3}	AsO_4^{-3}
Ag^+	Hg^{+2}	Bi^{+3}	MoO_4^{-2}
Tl^+	Mg^{+2}	La^{+3}	VO_3^-

The color obtained with scandium resembled that with zirconium, titanium, thorium, and the rare earths closely enough so that it was deemed necessary to establish the feasibility of separating them from scandium. Accordingly, 0.1M solutions of zirconyl nitrate, sodium titanate, thorium nitrate, and rare earth nitrates were chromatographed and then compared with the results obtained when these same solutions were mixed with scandium nitrate. Separations were effected in all cases with a 30 cm solvent run. The R_F values based on 25 runs for scandium and 10 runs for the other elements are given in Table III.

TABLE III

THE R_F VALUES OF IONS GIVING THE SAME COLOR WITH QUINALIZARIN

Thorium	0.77	
Scandium	0.57	
Rare earths	0.39	
Titanium	0.38	
Zirconium	0.30	(All values ±0.02)

Scandium is accordingly readily distinguishable in the presence of ions giving a similar color. A practical limit of sensitivity was found to be $1 \cdot 10^{-4}$ moles of scandium. This corresponds to a 0.01M concentration in the test solutions since the volume used on the paper strip was limited to 0.01 ml to avoid edge effects. Scandium was barely detectable when the test solution was 0.005M. There was no discernible coloration when 0.001M test solutions were used.

Several experiments were made using methanol 1M with respect to hydrogen chloride for the solvent. An R_F value of 0.75 for scandium was observed, using a 15 cm solvent run by upward diffusion. Separation of scandium from other elements was not tried with this solvent.

In testing various ores for scandium content the sample was decomposed by a method suitable to the particular ore, sodium carbonate fusion in most cases, and then extracted with nitric acid. The extract was evaporated to dryness and redissolved in 0.01M nitric acid. Scandium oxide added to various samples of ores was found to be completely removed by this treatment. A few of the samples

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examined required a slightly higher acid concentration to keep all of the salts in solution. An approximate quantitative estimation of the amount of scandium was made by treating a 450 mg sample of the ore as outlined above and dissolving in 1 ml of 0.01*M* nitric acid. Under these conditions a sample of ore containing 1% scandium would contain 4.5 mg of scandium per ml and would be 0.1*M* with respect to this element. Since 0.01*M* scandium solutions gave readily detectable chromatographs, samples of ore having as little as 0.1% scandium gave positive results.

Spectrographic examination of twenty-five samples of ores, principally from the United States and Canada, gave positive indication of scandium in three cases. Paper chromatography indicated scandium in the same ores with the results being considerably more definite.

SUMMARY

Scandium was readily detected by paper chromatography using methyl acetate as the solvent and quinalizarin for the developer. The reddish-violet color formed with scandium resembled the colers obtained with thorium, titanium, zirconium and the rare earths, but the difference in R_F values gave definite separation of these elements. Positive chromatographs were obtained by using 0.01 ml of solution 0.005*M* respect to scandium.

RÉSUMÉ

Le scandium peut être décelé facilement par chromatographie sur papier, en utilisant l'acétate de méthyle comme solvant et la quinalizarine comme réactif. La coloration rouge violet obtenue avec le scandium ressemble aux colorations obtenues avec le thorium, le titane, le zirconium et les terres rares; mais les valeurs de R_F sont suffisamment différentes pour permettre une séparation de ces éléments. Des chromatogrammes positifs ont été obtenus avec 0.01 ml d'une solution 0.005*M* en scandium.

ZUSAMMENFASSUNG

Mit Methylacetat als Lösungsmittel und Chinalizarin als Reagens kann Scandium papierchromatographisch nachgewiesen werden. Die hierbei auftretende rötlich-violette Färbung ist den durch Thorium, Titan, Zirconium und die seltenen Erden hervorgerufenen Farben ähnlich, aber die Verschiedenheit der R_F-Werte ist genügend gross, um eine Trennung der Elemente zu gestatten. Mit 0.01 ml einer 0.005*M* Scandiumlösung wurden positive Chromatogramme erhalten.

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PAPER CHROMATOGRAPHY OF INORGANIC IONS
VII. THE PAPER CHROMATOGRAPHY OF GERMANIUM

by

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In a recent review of the applications of chromatography to radiochemistry[1] we were able to discuss the significance of the R_F value of metals as a general property and for the solvent butanol saturated with 1N HCl, the R_F values of all B group elements of the periodic table except Ge were taken into consideration. Ge, being an exceedingly rare element, had not been studied.

It was recently suggested to us by Madame H. LANGEVIN to study the separation Ge — As with a view to preparing carrier-free As by bombardment of germanium metal. Thus this work was undertaken both to fill the gap in the R_F table of elements and to develop a method for the separation of Ge and As.

In the preparation of a solution of Ge(IV) from Ge metal we used a fusion with NaOH, as the attack with aqua regia does not proceed quickly and after several hours the solution obtained does not permit detection of Ge. The fusion mixture was dissolved in a small quantity of water and an excess of aqua regia added to ensure conversion to Ge(IV).

The spots of Ge may be detected in several ways:

1) Spraying with ammonium molybdate solution followed by sodium stannite in 5N NaOH produces a sensitive blue reaction. In acid medium no blue colour could be obtained either with benzidine nor with stannous chloride as reductant.

2) 8-hydroxyquinoline produces in ultraviolet light a pale green fluorescent spot. This reaction is best carried out by dipping the paper strip after drying into an alcoholic ammoniacal solution of 8-hydroxyquinoline and viewing immediately under ultraviolet light.

3) The paper is exposed to H_2S fumes and dried in a current of warm air till it does not smell of H_2S. In this treatment both Ge(IV) and As(III) form sulphides; the first colourless and the second pale yellow. If the paper strip is subsequently bathed in a N/100 solution of $AgNO_3$ the more insoluble black Ag_2S is formed on the spots where the Ge and As sulphides are situated. Thus black spots on a white background are distinctly visible for about fifteen minutes after which time there is a darkening of the paper.

The spots of the Ge solution prepared by fusion as mentioned above were placed on Whatman No. 1 sheets and developed by the ascending method with butanol saturated with 1*N* HCl.

The pure solution yielded spots with R_F 0.35 - 0.40 with reference to the water front, and 0.25 - 0.29 with reference to the first liquid front. When shown up with 8-hydroxyquinoline a spot due to Ni (R_F 0.1) and one weak spot due to Fe (R_F 0.15) were also revealed and are due to Ni and Fe introduced by fusing in a nickel crucible. A solution of arsenite and arsenate mixed with the germanium solution produced three well separated bands As(V) R_F 0.84, As(III) R_F 0.52 and Ge(IV) R_F 0.26. Thus an adequate R_F difference for radiochemical separation exists between Ge and As.

SUMMARY

Germanium(IV) may be separated from As and many other elements by paper chromatography with butanol saturated with 1*N* HCl. The R_F value of germanium (IV) is 0.25 - 0.29.

RÉSUMÉ

Le germanium(IV) peut être séparé de l'arsenic et de beaucoup d'autres éléments par chromatographie sur papier, au moyen de butanol saturé de HCl *N*. Le R_F du germanium(IV) est 0.25 - 0.29.

ZUSAMMENFASSUNG

Das Germanium(IV) kann vom Arsen und von vielen andern Elementen durch Papierchromatographie abgetrennt werden mit Hilfe von Butanol, das mit HCl *N* gesättigt ist. Für Germanium(IV) ist R_F 0.25 - 0.29.

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SÉPARATION Ba^{+2} — Sr^{+2} SUR COLONNE D'ÉCHANGEUR D'IONS

par

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INTRODUCTION

Dans la littérature, on signale deux procédés de séparation Ba^{+2}/Sr^{+2} sur échangeurs d'ions:

1. la séparation du ^{140}Ba et du $^{89-90}Sr$ sur colonne d'Amberlite I.R.1 (40-60 mesh), par élution avec une solution d'acide citrique 0.26*M* à pH 5.0[1].
2. la séparation du ^{140}Ba et du $^{89-90}Sr$ sur colonne de Dowex 50 colloïdal, par élution avec une solution d'acide citrique 0.5*M* à pH 7.5-8.0[2].

Les considérations théoriques sur le phénomène d'échange montrent que, dans le cas de l'élution avec une solution complexante, le facteur de séparation de deux ou plusieurs ions de même valence augmente avec la valeur du rapport des constantes de stabilité des complexes formés[3].

Si l'on compare les valeurs connues des constantes de différents complexants pour les ions Ba^{+2} et Sr^{+2}, on trouve qu'à l'heure actuelle, c'est le complexon — acide éthylènediaminotétraacétique — qui se présente le plus favorablement.

Complexant	$pK_{Ba^{+2}}$	$pK_{Sr^{+2}}$	Δ pK
Acide oxalique	2.3	2.5	— 0.2
Acide méthylaminodiacétique	2.6	2.8	— 0.2
Acide aminotriacétique	4.8	5.0	— 0.2
Acide éthylènediaminotétraacétique	7.76	8.63	— 0.87
Acide citrique	2.3	2.8	— 0.5

Il nous a paru intéressant, dans ces conditions, d'examiner les ressources offertes par le complexon pour la séparation du baryum et du strontium sur colonne d'échangeur d'ions.

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Le présent travail décrit les résultats de séparations obtenus sur des mélanges Ba^{+2} — Sr^{+2} synthétiques en quantités pondérables; nous nous proposons, dans la suite, d'essayer d'appliquer la méthode à la séparation de ces deux radioéléments produits dans la fission de l'uranium.

DÉTAILS EXPÉRIMENTAUX

a) Nous disposions, pour cette étude, de $Ba^*(NO_3)_2$ et de Sr^*Cl_2 radioactifs produits par irradiation à la pile de Harwell; il s'agit du ^{131}Ba donnant le ^{131}Cs comme produit de filiation et du ^{89}Sr.

Les caractéristiques radioactives de ces éléments sont résumées dans le tableau suivant :[4,5].

		^{131}Ba	^{131}Cs	^{89}Sr
Périodes		12 jours	10.2 jours	53 jours
Rayonnements	β	—	—	1.5 Mev
,,	γ	0.26; 0.5; 1.2 Mev	—	—
,,	X	31.5 Kev	31.0 Kev	—
,, ē conversion		0.24; 0.42 Mev*	—	—

* Ces valeurs correspondent avec les valeurs du rayonnement γ: 0.5 et 0.26 Mev.

Nous nous sommes assurés de la pureté radiochimique de ces préparations, en déterminant les valeurs de leurs composantes énergétiques par mesure de l'absorption de leur rayonnement à travers du plomb ou de l'aluminium.

Le Ba a été débarrassé de son produit de filiation par précipitation du Ba sous forme de nitrate par HNO_3 fumant après addition de Cs comme entraîneur[5].

Pour doser le Ba et le Sr l'un en présence de l'autre, nous avons établi des courbes d'absorption de leurs rayonnements à travers l'aluminium pour des mélanges où ces radioéléments intervenaient en proportions connues.

Lors des essais avec la résine, le Ba et le Sr se trouvaient sous forme de nitrate·

b) La résine utilisée est le Dowex 50 (250-500 mesh) sous forme sodique; elle a été préparée par lavage de la résine acide par une solution de NaCl à 10% jusqu'à pH supérieur à 4 et par lavage à l'eau distillée jusqu'à neutralité et disparition des ions Cl^-.

Elle est séchée à l'étuve à 110° C[6].

La capacité ionique de la résine est de 5.2 milliéquivalents/g.

c) Les solutions complexantes utilisées pour les différentes expériences ont été préparées à partir du sel disodique de l'acide éthylènediaminotétraacétique

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$Na_2H_2Y.2H_2O$ (complexon III) et amenées au pH convenable par addition d'hydroxyde de sodium ou d'acide nitrique. Les essais statiques de partage comme les séparations sur colonne ont été faits au moyen de solutions de complexon de l'ordre de $10^{-2}M$.

d) Les essais statiques d'échange de Ba^{+2} ou Sr^{+2} entre la résine et la solution de complexon ont été faits de la façon suivante:

1 gramme de Dowex 50, sous forme sodique, séché à 110° C est mis en contact avec 50 ml de solution $0.8 \cdot 10^{-2}M$ en complexon et de l'ordre de $10^{-2}M$ en métal. La préparation est maintenue pendant 12 heures au moins en thermostat à 26° C. Après cela, un volume déterminé de la phase aqueuse est prélevé et le baryum (ou le strontium) y est dosé radiochimiquement; le métal fixé sur la résine est déterminé par différence avec l'activité initiale mise en jeu.

e) La colonne servant aux séparations chromatographiques a 19 cm de hauteur et 1 cm² de section; elle contient environ 10 g de résine; celle-ci est d'abord lavée avec la solution de complexon qui servira à l'élution, jusqu'à ce que le pH ne soit plus modifié par passage sur la colonne. On y verse ensuite le mélange $Ba^{+2} + Sr^{+2}$ mis en solution dans un petit volume de la solution éluante; lorsque le niveau du liquide est près d'affleurer la surface de la résine, on fait arriver la solution complexante pour l'élution. L'éluat est recueilli au moyen d'une fractionneuse automatique; les fractions recueillies sont évaporées au moyen d'une lampe infra-rouge et les résidus sont passés au compteur. Les essais ont été faits en variant soit le pH de la solution éluante soit la vitesse d'élution.

Toutes les mesures d'activité ont été faites au moyen d'un tube G.M. de la firme Tracerlab T.G.C.2 (les mesures relatives au Cs avec un tube T.G.C.3) et une installation de comptage Nuclear.

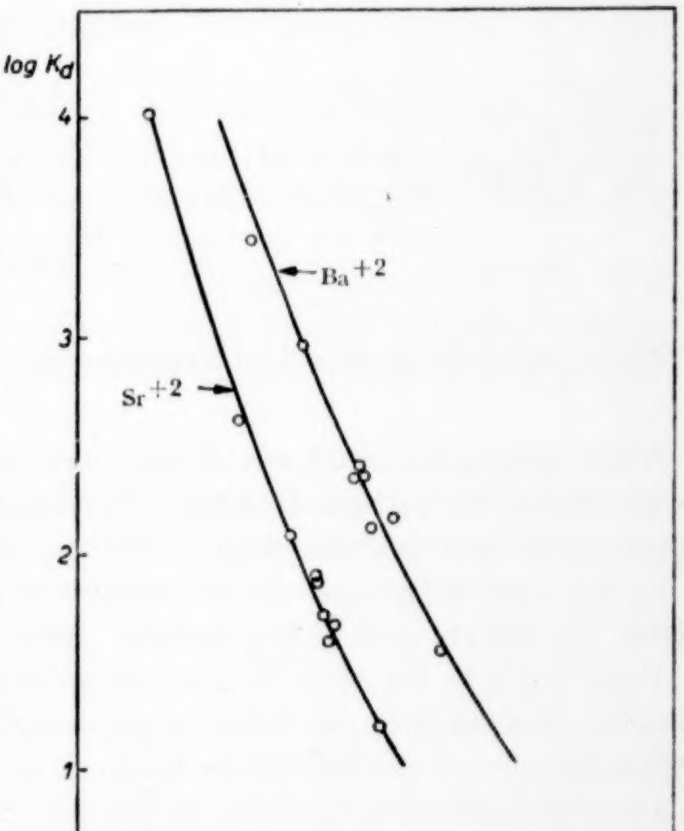

Fig. 1. Courbe de K_d en fonction du pH en milieu complexon III.
o : Points expérimentaux
— : Courbe théorique calculée avec les constantes A suivantes:
Ba^{+2}: 4.76
Sr^{+2}: 4.62

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ÉQUILIBRE DE PARTAGE

L'équilibre de partage du cation entre la résine et la solution est représenté par le coefficient de partage K_d:

$$K_d = \frac{[MR_n]}{[M^{+n}]_t} \text{ ml/g de résine} \qquad (1)$$

$[MR_n]$: ion-g du cation M^{+n}/g de résine.
$[M^{+n}]_t$: ion-g du cation M^{+n} (complexé et libre)/ml de solution.

Les valeurs des coefficients de partage obtenus à différents pH sont représentées dans la Fig. 1 et les valeurs numériques se trouvent dans la deuxième colonne des Tableaux I et II.

TABLEAU I

STRONTIUM: $[Sr^{+2}]_{init} = 0.21 \cdot 10^{-2} M$ $[compl.]_t = 0.8 \cdot 10^{-2} M$
$m = 1$ g $v = 50$ ml $t = 26°$ C

pH équil.	log K_d exp.	log β calc.	log $K_d°$	log $K_{d\,calc.} = 4.62 + \log \beta$
9.7	0.8 *	—	—	—
9.45	0.0	—	—	—
7.25	1.19	— 3.45	4.64	1.17
6.85	1.66 *	— 3.01	4.67	1.61
6.8	1.59	— 2.95	4.54	1.67
6.75	1.71	— 2.89	4.60	1.73
6.7	1.89 *	— 2.83	4.72	1.79
6.45	2.08	— 2.52	4.60	2.1
6.0	2.61	— 1.90	4.51	2.72
5.2	4.02 *	— 0.60	4.62	4.02
			Moy.: 4.62	

* Ces déterminations ont été faites à $t°$ ordinaire.

TABLEAU II

BARYUM: $[Ba^{+2}]_{init} = 0.18 \cdot 10^{-2} M$ $[compl.]_t = 0.8 \cdot 10^{-2} M$
$m = 1$ g $v = 50$ ml $t = 26°$ C

pH équil.	log. K_d exp.	log β calc.	log $K_d°$	log $K_{d\,calc.} = 4.76 + \log \beta$
7.82	1.54	— 3.18	4.72	1.58
7.4	2.15	— 2.76	4.91	2.00
7.20	2.10	— 2.52	4.62	2.24
7.15	2.36	— 2.48	4.84	2.28
7.10	2.40	— 2.42	4.82	2.34
7.05	2.34	— 2.37	4.71	2.39
6.58	2.95	— 1.81	4.76	2.95
6.12	3.43	— 1.18	4.61	3.58
			Moy.: 4.76	

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La variation du coefficient de partage avec le pH de la solution peut s'interpréter quantitativement d'après la loi d'action de masses; en effet, l'équation d'équilibre appliquée à la réaction ionique d'échange

$$n\mathrm{R\,Na} + \mathrm{M}^{+n} \rightleftarrows \mathrm{M\,R_n} + n\,\mathrm{Na}^+ \quad \ldots\ldots\ldots \quad (2)$$

est

$$\frac{(a_{\mathrm{Na}^+})^n\,(a_{\mathrm{MR_n}})}{(a_{\mathrm{M}^{+n}})\;(a_{\mathrm{R\,Na}})^n} = K_{\mathrm{ex}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

a: représentant les activités.

En introduisant les coefficients d'activité f, l'équation (3) peut s'écrire:

$$\frac{[\mathrm{Na}^+]^n\,[\mathrm{M\,Rn}]}{[\mathrm{M}^{+n}]\,[\mathrm{R\,Na}]^n} = K_{\mathrm{ex}}\,\frac{f_{\mathrm{M}^{+n}}\cdot f^n_{\mathrm{RNa}}}{f^n_{\mathrm{Na}^+}\cdot f_{\mathrm{MRn}}} = K_m \quad \ldots\ldots\ldots \quad (4)$$

Si l'on a affaire à des équilibres d'échange en solution aqueuse de force ionique constante et si la quantité de M^{+n} mise en jeu est très faible vis-à-vis de la quantité de résine, il semble que l'on puisse, en première approximation, admettre que K_m est une constante, uniquement fonction de la température.

Il en résulte qu'en l'absence d'une substance complexante dans la solution on a:

$$K_d^\circ = K_m \cdot \frac{[\mathrm{R\,Na}]^n}{[\mathrm{Na}^+]^n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

Dans ces conditions, si la quantité initiale de M^{+n} en solution est négligeable vis-à-vis de la quantité d'ions échangeables par la résine, K_d peut être considéré comme une constante indépendante de la concentration initiale en M^{+n}.

Tenons compte maintenant des équilibres supplémentaires introduits par la présence en solution de complexon.

Les pK du complexon déterminés par SCHWARZENBACH ET ACKERMANN[7] sont:

$\mathrm{p}K_1 = 1.1996$ $\mathrm{p}K_2 = 2.672$ $\mathrm{p}K_3 = 6.161$ $\mathrm{p}K_4 = 10.26$.

1er cas: Complexon (HY_4) *en excès par rapport à* M^{+n}

Dans ces conditions,

$$[\mathrm{compl.}]_t = [\mathrm{Y}^{-4}] \times \Theta \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

$$\text{avec } \Theta = \left\{ 1 + \frac{[\mathrm{H}^+]}{K_4} + \frac{[\mathrm{H}^+]^2}{K_4\;K_3} + \frac{[\mathrm{H}^+]^3}{K_4\;K_3\;K_2} + \frac{[\mathrm{H}^+]^4}{K_4\;K_3\;K_2\;K_1} \right\}$$

Le Ba^{+2} et le Sr^{+2} forment avec le complexon les deux complexes suivants avec les constantes de stabilité déterminées par SCHWARZENBACH[7]:

$$\begin{array}{ll} Ba^{+2} + Y^{-4} \rightleftarrows BaY^{-2} & K^{1}_{\text{compl.}} = 10^{-7.76} \\ Ba^{+2} + HY^{-3} \rightleftarrows BaHY^{-} & K^{2}_{\text{compl.}} = 10^{-2.07} \\ & \\ Sr^{+2} + Y^{-4} \rightleftarrows SrY^{-2} & K^{1'}_{\text{compl.}} = 11^{-8.63} \\ Sr^{+2} + HY^{-3} \rightleftarrows SrHY^{-} & K^{2'}_{\text{compl.}} = 10^{-2.30} \end{array} \quad \ldots\ldots \quad (7)$$

Nous allons négliger, en première approximation, la formation des complexes Ba HY⁻ et SrHY⁻.

Dans ces conditions, on peut écrire:

$$\frac{[M^{+2}]}{[MY^{-2}]} = \frac{K_{\text{compl.}}}{[Y^{-4}]} = \frac{K_{\text{compl.}}\,\Theta}{[\text{compl.}]_t} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

ou encore:

$$\frac{[M^{+2}]}{[M^{+2}]_t} = \frac{K_{\text{compl.}} \times \Theta}{K_{\text{compl.}} \times \Theta + [\text{compl.}]_t} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

Le coefficient de partage vaut donc:

$$K_d = \frac{[MR_2]}{[M^{+2}]_t} = \frac{K_{\text{compl.}} \times \Theta}{K_{\text{compl.}} \times \Theta + [\text{compl.}]_t}\, K_m\, \frac{[NaR]^2}{[Na^+]^2} \quad \ldots\ldots \quad (10)$$

Posons:

$$\beta = \frac{1}{1 + \dfrac{[\text{compl.}]_t}{K_{\text{compl.}} \times \Theta}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

L'équation (10) s'écrit:

$$K_d = \beta .\, K_m\, \frac{[NaR]^2}{[Na^+]^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

2ème cas: Complexon non en excès par rapport à M^{+n}

Dans ce cas, l'équation (6) doit être remplacée par la suivante:

$$[\text{compl.}]_t = [Y^{-4}] \times \Theta + [MY^{-2}] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

En tenant compte de l'équilibre du complexe, l'équation (13) devient:

$$[\text{compl.}]_t = [Y^{-4}] \left\{ \Theta + \frac{[M^{+2}]}{K_{\text{compl.}}} \right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

En éliminant $[Y^{-4}]$ entre (13) et (14), on trouve:

$$[MY^{-2}] = \frac{[M^{+2}]\ [\text{compl.}]_t}{K_{\text{compl.}} \times \Theta + [M^{+2}]} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

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La quantité totale de cation M^{+2} intervenant vaut:

$$M_t = v\,[M^{+2}]\left\{1 + \frac{[\text{compl.}]_t}{K_{\text{compl.}} \times \Theta + [M^{+2}]}\right\} + m\,[MR_2] \quad \ldots\ldots\ldots \quad (16)$$

v et m représentant respectivement le volume et la masse de la résine.

Nous avons deux équations (15) et (16) permettant de calculer $[MR_2]$ et $[M^{+2}]$ en fonction des quantités connues M_t, $[\text{compl.}]_t$, $K_{\text{compl.}}$, Θ, K_m, $\frac{[RNa]}{[Na^+]}$ et par conséquent permettant, en principe, de calculer K_d en fonction de ces mêmes grandeurs.

En vue d'interpréter les résultats expérimentaux, nous allons considérer les solutions approximatives suivantes:

1. Le pH est suffisamment élevé pour que pratiquement tout le métal soit en solution, l'équation (16) se simplifie alors:

$$\frac{M_t}{v} = [M^{+2}]_t = [M^{+2}]\left\{1 + \frac{[\text{compl.}]_t}{K_{\text{compl.}} \times \Theta + [M^{+2}]}\right\} \quad \ldots\ldots\ldots \quad (17)$$

Dans notre cas particulier, 1 est négligeable devant

$$\frac{[\text{compl.}]_t}{K_{\text{compl.}} \times \Theta + [M^{+2}]} \quad \text{si bien que} \quad [M^{+2}] = \frac{[M^{+2}]_t \times K_{\text{compl.}} \times \Theta}{[\text{compl.}]_t - [M^{+2}]_t} \qquad (18)$$

d'où

$$K_d = \frac{K_{\text{compl.}} \times \Theta}{[\text{compl.}]_t - [M^{+2}]_t} \cdot K_m \frac{[NaR]^2}{[Na^+]^2} \quad \ldots\ldots\ldots\ldots \quad (19)$$

2. Aux faibles pH, tout le métal se trouve pratiquement sur la résine et, dans ces conditions, on se trouve dans le cas du complexon en excès traité ci-dessus et le K_d est donné par la formule (10).

En conclusion, le coefficient de partage en présence de complexon est égal au coefficient de partage sans complexon multiplié par un facteur β, fonction du pH, ce facteur β vaut:

1°. en présence d'un excès de complexon par rapport au cation envisagé (équations 10 et 11)

$$\beta = \frac{1}{1 + \dfrac{[\text{compl.}]_t}{K_{\text{compl.}} \times \Theta}}$$

2°. en présence de complexon non en excès

a) pH élevés: (équation 19)

$$\beta = \frac{K_{\text{compl.}} \times \Theta}{[\text{compl.}]_t - [M^{+2}]_t}$$

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b) pH faibles: (équations 10 et 11)

$$\beta = \frac{1}{1 + \dfrac{[\text{compl.}]_t}{\text{K}_{\text{compl.}} \times \Theta}}$$

La Fig. 2 représente les courbes de log β en fonction du pH, calculées par les formules ci-dessus pour une concentration de complexon $[\text{compl.}]_t = 0.8 \cdot 10^{-2} M$ dans les deux cas envisagés

a) le Ba^{+2} et le Sr^{+2} sont en dose traceur (courbes 2 et 2').

b) $[Ba^{+2}]_{\text{init.}} = 0.18 \cdot 10^{-2}$ ion-g/l, $[Sr^{+2}]_{\text{init.}} = 0.21 \cdot 10^{-2}$ ion g/l (courbes 1 et 1').

Il nous reste maintenant à comparer les données expérimentales avec les formules que nous venons d'établir; elles montrent que log K_d est égal à log β à une constante près (le log K_d° en l'absence de complexon):

$$\log K_d = \log \beta + \log \left(K_m \frac{[\text{NaR}]^2}{[\text{Na}^+]^2} \right) \quad \ldots\ldots\ldots\ldots\ldots \quad (20)$$

Les Tableaux I et II contiennent pour le Ba^{+2} et le Sr^{+2} les valeurs expérimentales de K_d (colonne 2), les valeurs de log β calculées d'après les formules (11) et (19) (colonne 3) ainsi que la différence log K_d — log β (colonne 4). On voit que, conformément aux formules établies ci-dessus, cette valeur de K_d° est constante, dans les limites des erreurs expérimentales. La dernière colonne du tableau donne les valeurs de log K_d calculé par la formule (20) en y introduisant la valeur moyenne trouvée pour K_d°; ces valeurs ont servi à tracer les courbes théoriques de la Fig. 1. Il est intéressant de conclure que l'accord entre les résultats expérimentaux et les formules théoriques est très satisfaisant.

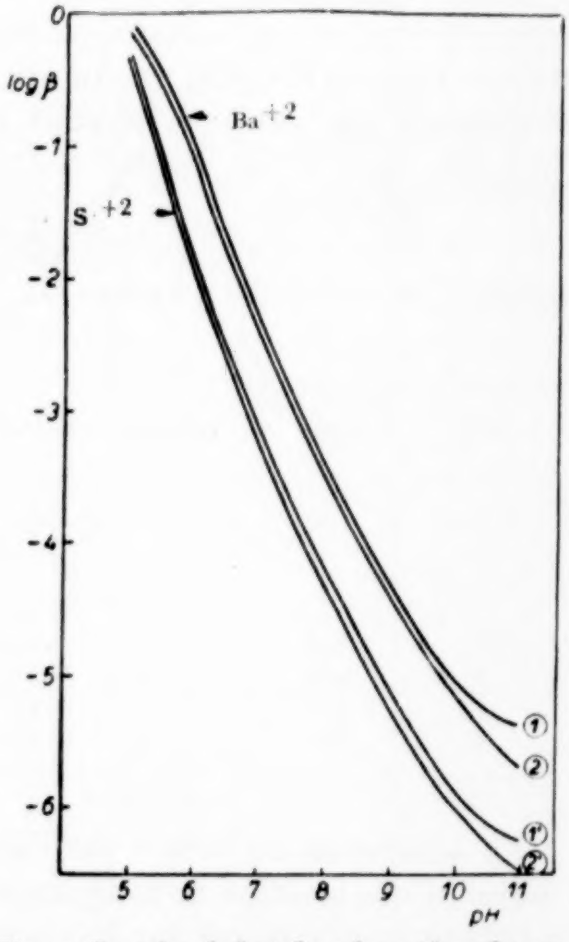

Fig. 2. Courbe de log β en fonction du pH
(1): $0.18 \cdot 10^{-2} M$ Ba^{+2}
$0.8 \cdot 10^{-2} M$ Complexon
(1'): $0.21 \cdot 10^{-2} M$ Sr^{+2}
$0.8 \cdot 10^{-2} M$ Complexon
(2) (2'): $0.8 \cdot 10^{-2} M$ Complexon (excès).

SÉPARATION Ba^{+2} — Sr^{+2} SUR COLONNE

La théorie de la séparation sur colonne montre que, dans le cas d'un mélange de deux cations de même valence par exemple, le rapport des coefficients de

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partage $\frac{K_d{}^1}{K_d{}^2} = \alpha$ (appelé facteur de séparation) est, toutes autres choses égales, une mesure de la séparation obtenue sur colonne; c'est-à-dire que, dans le cas particulier envisagé ici, le facteur de séparation est donné directement à une constante près, sur la Fig. 1, en effet:

$$\log \alpha = \log \beta_{Ba^{+2}} - \log \beta_{Sr^{+2}} + \log \frac{K_m{}^{Ba^{+2}}}{K_m{}_{Sr^{+2}}} \quad \ldots\ldots\ldots \quad (21)$$

avec $\log \frac{K_m{}^{Ba^{+2}}}{K_m{}_{Sr^{+2}}} = 0.14$.

dans les conditions expérimentales en question.

On voit donc, d'après la Fig. 1 ou 2, que le facteur de séparation faible en l'absence de complexon ou en milieu acide avec complexon, augmente progressivement vers les pH alcalins; cela montre de façon tangible l'intérêt des complexants pour la séparation des cations sur colonne de résine.

Nous avons effectué quelques essais de séparation en modifiant soit le pH du milieu éluant, soit la vitesse d'élution; les données expérimentales sont consignées dans le Tableau III (Fig. 3). Au cours de ces essais, nous n'avons pas pu mettre en évidence le Cs, son activité était trop faible.

TABLEAU III

[compl.] = $10^{-2}M$; 10 g Dowex 50. (R Na. 250-500 mesh) colonne 19 cm hauteur, 1 cm² section

No.	pH	vitesse ml/cm²/min.	$Ba^{+2}_{ion\text{-}g}$	$Sr^{+2}_{ion\text{-}g}$	
1	7.4	1.3	10^{-4}	10^{-4}	Le Ba^{+2} a été élué à pH = 11.5
2	8.8	0.14	$2.5 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$	
3	9.0	0.1	$2.5 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$	
4	9.0	0.16	$2.5 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$	
5	9.0	0.43	$2.5 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$	

La séparation Ba^{+2}/Sr^{+2} sur Dowex 50 peut donc s'effectuer par élution au moyen d'une solution de complexon et on peut régler dans une certaine mesure la séparation en agissant sur le pH et la vitesse d'élution.

Plusieurs auteurs ont montré que les séparations sur échangeurs d'ions donnent encore des résultats satisfaisants lorsqu'on a affaire à des teneurs impondérables; nous nous proposons d'examiner les possibilités de ce milieu éluant pour la séparation de ces deux radioéléments de fission sans entraîneur.

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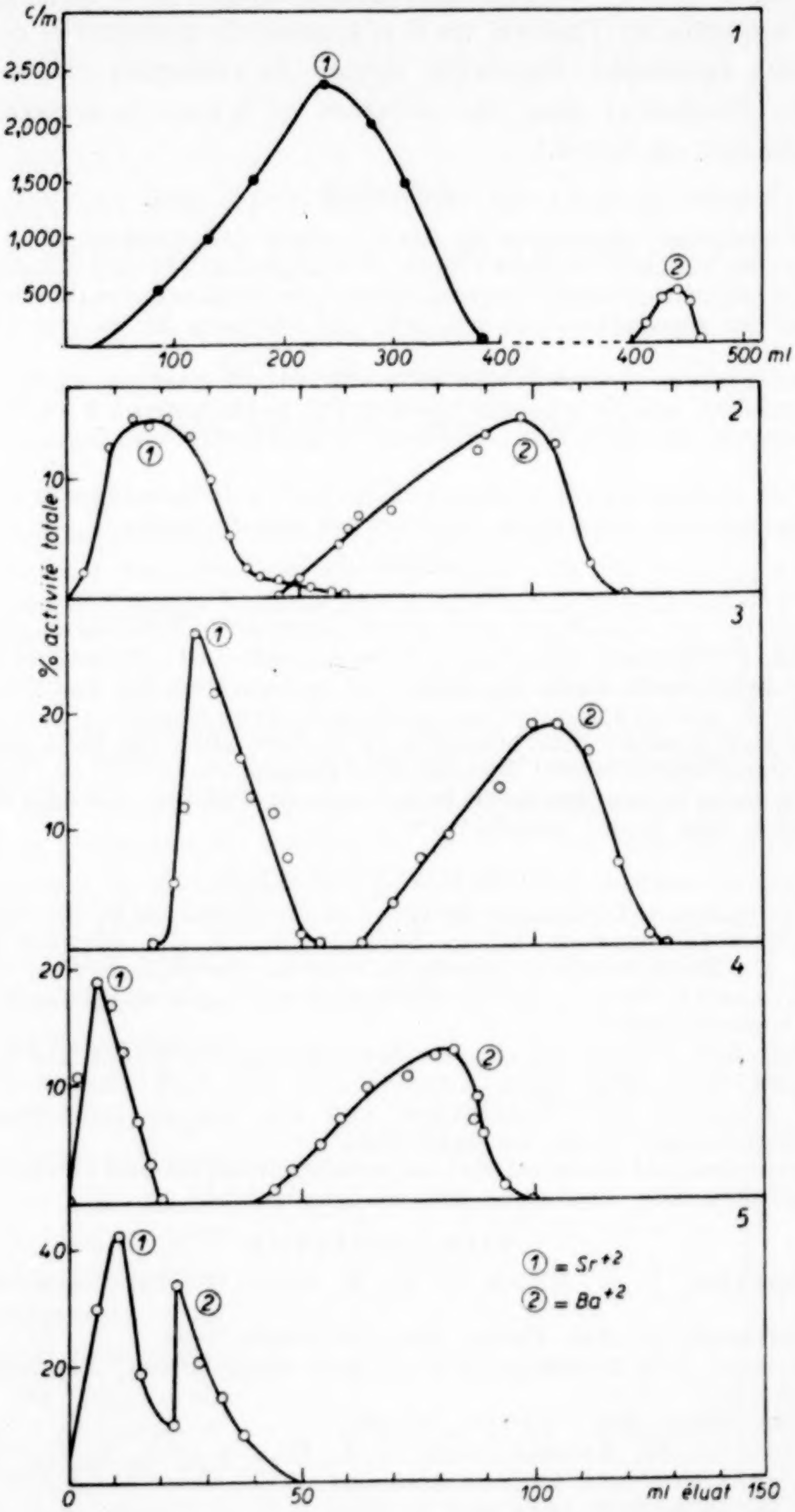

Fig. 3. Courbes d'élution Ba^{+2}/Sr^{+2} dans les conditions indiquées dans le Tableau III.

L'un de nous (R.B.) se plaît à remercier Monsieur le professeur Gueben pour l'aide apportée et l'intérêt qu'il n'a cessé de marquer à ce travail.

Nous avons également l'agréable devoir de remercier vivement l'Institut des Sciences Nucléaires pour les subsides qu'il nous a accordés et qui ont permis d'effectuer ce travail.

RÉSUMÉ

Il s'agit d'essais de séparation de Ba^{+2} — Sr^{+2} (de l'ordre de $2.5\cdot10^{-5}$ ion-g) sur Dowex 50 en utilisant comme éluant le complexon III (sel disodique de l'acide éthylènediaminotétraacétique). Les essais statiques de partage entre résine et solution, de même que les séparations sur colonne, ont été faits au moyen de Ba et de Sr radioactifs.

Les essais statiques montrent que le coefficient de partage varie très fortement avec le pH suivant une courbe qui s'interprête parfaitement à partir des données physico-chimiques relatives au complexon et aux complexes formés avec les deux cations.

Des essais de séparation sur colonne ont été faits à différents pH et avec différentes vitesses d'élution. La séparation est trouvée satisfaisante.

SUMMARY

Separation tests of Ba^{+2} — Sr^{+2} (in the amount of $2.5\cdot10^{-5}$ ion-g) on Dowex 50 using Complexon III (disodium salt of ethylenediaminetetra-aceticacid) as eluant, are dealt with. Static tests of partition between resin and solution, as well as column separations, have been made by means of radioactive Ba and Sr.

Static tests show that the partition coefficient varies greatly with the pH according to a curve which is easily interpreted from physico-chemical data relative to complexon and complexes formed by the two cations.

Separation tests on column have been made at different pH and elution speeds. The separation was found satisfactory.

ZUSAMMENFASSUNG

Es handelt sich um Trennungsproben von Ba^{+2} und Sr^{+2} (in der Grösse von $2.5\cdot10^{-5}$ Ion/g) auf Dowex 50, indem Komplexon III (Di-Natrium-Äthyldiaminotetraacetat) als Elutionsmittel gebraucht wurde. Die statistischen Teilungsproben zwischen Harz und Lösung, sowie die Teilungen auf Säule wurden mit radioaktivem Ba und Sr unternommen.

Die statistischen Proben zeigen, dass der Teilungskoeffizient durch das pH stark geändert wird und zwar nach einer Kurve die sich aus den physikalisch-chemischen Angaben über Komplexon und die mit zwei Kationen gebildeten Komplexverbindungen leicht auslegen lässt.

Trennungsproben auf Säule wurden zu verschiedenen pH und Elutionsgeschwindigkeiten ausgeführt. Die Trennung galt als genügend.

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THE SEPARATION OF LANTHANUM AND ACTINIUM BY CONTINUOUS PAPER ELECTROPHORESIS

by

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Separations employing an electric field at right angles to a flowing liquid inside a porous medium have been realized by SVENSSON AND BRATTSTEN[1] and later by other workers[2,3,4]. Inorganic compounds were first separated in this manner by STRAIN and coll[5].

The separation of various rare earth mixtures employing electrophoresis on paper strips without simultaneous flow of the electrolyte has been recorded using citric acid[6] as well as lactic and tartaric acid[7] as electrolyte. The quantities that may be handled on paper strips are relatively small hence the separation of a trace from large quantities of another element is not easy to realize. It thus appeared of interest to investigate the possibilities of continuous paper electrophoresis for the separation of Ac from La as besides the ion-exchange method of YANG AND HAISSINSKY[8] no satisfactory methods are available.

The apparatus used was constructed after the design of DURRUM[3] with electrodes at the lower ends of the paper only. This apparatus is shown schematically in Fig. 1. Although this technique produces a smaller separation effect for a given potential than electrodes applied right along the edges of the paper, its simplicity and absence of electrolysis products on the paper more than balance this disadvantage.

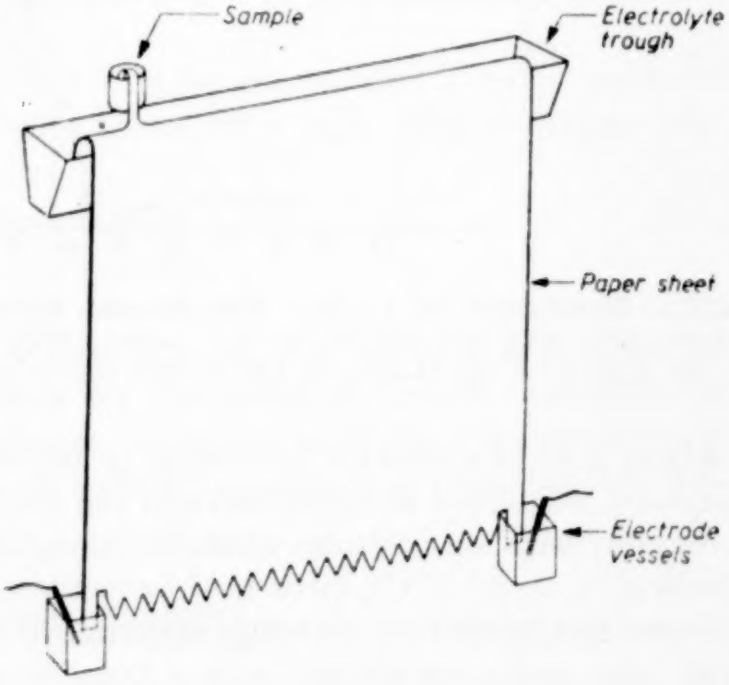

Fig. 1. The apparatus (schematic).

Before working with the valuable Ac concentrates at our disposal, trials were conducted with mixtures of Y and La and of Nd and Pr to find suitable conditions for the separation. When using 1% citric acid (1g hydrated citric acid per 100 ml of water), the electrolyte employed previously on paper strips[6], the application of 300 V on Whatman No. 1 sheets of the dimension shown in Fig. 2 yields separations comparable to those on paper strips.

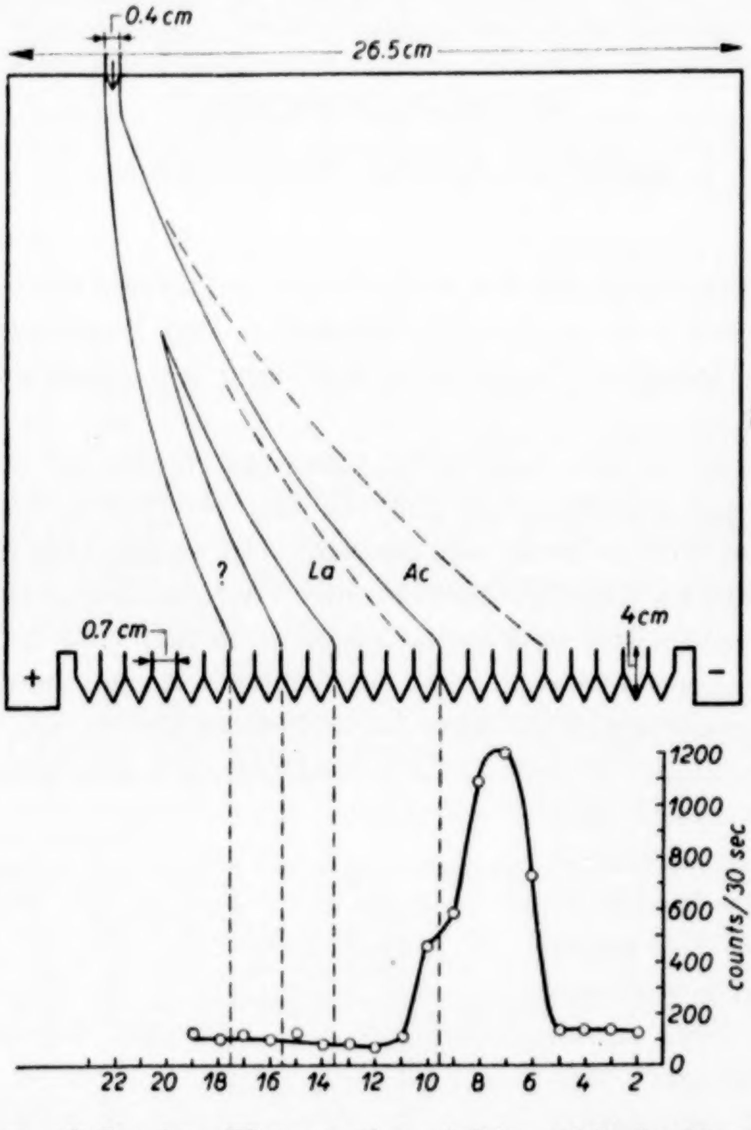

Fig. 2. Separation of La-Ac. The tracks visible with hydroxyquinoline under ultraviolet light are drawn on the paper sheet. Ac was detected by the activity of the fractions, as shown in the graph below the diagram of the paper sheet.

About 3 ml of a solution containing 30 mg of rare earths may be separated in five days. The speed of separation and the quantity of citric acid used compares favourably with ion exchange methods. 30 mg of rare earths, after separation, are dissolved in 20 ml of 1% citric acid *i.e.* contaminated with 200 mg of citric acid, whereas, in a typical ion exchange experiment[9] with 5% citrate, 15 mg Ce (or any other rare earth) are diluted with 4 litres of solvent containing 200 g of citric acid. The time required for continuous electrophoretic separation is comparable to ion exchange elution at 100° C and only a fraction of the time required for ion exchange chromatography at room temperature. In these comparisons it should however be remembered that electrophoresis has a much more limited scope than ion exchangers and not all mixtures of rare earths may be separated.

EXPERIMENTAL

The La-Ac mixture (or rare earth mixture) was dissolved in HCl precipitated with NH_4OH, the precipitate washed with distilled water and then dissolved on the water bath in 1% citric acid. The paper sheets were cut in the shape shown in Fig. 2, the upper end hung into the trough and the tongues placed into the respective funnels or test tubes. The electrolyte was allowed to run down to the bottom of the sheet, then the electrode vessels filled with the same electrolyte and the tongue at the top of the sheet introduced into the beaker containing the sample to be separated and the current switched on (at 300 V the current is about 10 mA).

The electrolyte runs down the paper at a rate of *ca.* 100 ml per day and the trough was replenished daily since the slow flow rate did not warrant a continuous feed. After six days the fractions were evaporated and the paper sprayed with alcoholic ammoniacal hydroxyquinoline to reveal the tracks of the macro components. A fluorescent band slower than La was detected in the La-Ac separation, which is probably another rare earth in small quantities.

The Ac was detected by the beta activity after evaporation and accumulation of derivatives and as shown on Fig. 2 the Ac is well separated from the La. Separations of mixtures of Y-La in equal amounts and of natural didymium proceeded also with a good degree of separation.

In both cases tracks on the paper were completely separated and the respective fractions yielded only single bands when tested with paper strip electrophoresis.

CONCLUSION

Continuous paper electrophoresis has been shown to be a method suitable for the separation of macro amounts of certain rare earth mixtures and of Ac from La.

The data available at present permit its application in certain cases only. In these cases however the method compares favourably with other techniques such as ion-exchange chromatography or fractional crystallisation, requiring less time and materials.

ACKNOWLEDGEMENT

The author wishes to thank Mme I. JOLIOT-CURIE and M. G. BOUISSIÈRES for valuable suggestions and advice.

References p. 148.

SUMMARY

A method has been worked out for the separation of La-Ac mixtures and certain rare earth mixtures by continuous electrophoresis on paper sheets using 1% citric acid as electrolyte and a potential of 300 V.

RÉSUMÉ

Une méthode a été établie, pour la séparation lanthane-actinium et quelques autres terres-rares, par électrophorèse continue sur papier, en présence d'acide citrique à 1%, comme électrolyte, et à un potentiel de 300 V.

ZUSAMMENFASSUNG

Es wurde eine Methode zur Trennung von La-Ac-Mischungen und Mischungen gewisser seltener Erden durch kontinuierliche Elektrophorese auf Papierbögen unter Verwendung von 1%iger Zitronensäure als Elektrolyt und einem Potential von 300 V ausgearbeitet.

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THE MICROCHEMICAL ELECTROLYTIC ANALYSIS OF ALLOYS IN HYDROCHLORIC ACID SOLUTIONS

I. BRASSES AND BRONZES

by

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The advantages of employing chloride solutions for quantitative electrolytic analysis are well established[1-6], but apart from preliminary investigations to which this work is a sequel and development [3,7]they have not been applied on **a** microchemical scale.

Throughout the work described in this paper the apparatus and techniques of separation by graded potential were as previously described by SAND AND LINDSEY[9].

PRELIMINARY INVESTIGATIONS

A preliminary investigation of the separation of copper from chloride solution by graded potential in the presence of antimony, tin, lead, zinc, aluminium and zinc and nickel was described in 1938[3]. As has been shown on a macro (1 g) scale[9] copper thus separated always contains antimony if this element also is present and must therefore be analysed further.

Tin and lead are separated together from hydrochloric acid solutions. In such solutions a high concentration of acid is necessary to prevent precipitation of the tin by hydrolysis and a copper coated cathode must be employed to reduce the deposition overpotential and to lessen the tendency for electrolytic re-solution of the deposit during washing. This loss is also minimized by neutralizing the liquid before washing. Tin solutions, even in the presence of much hydrochloric acid are not stable for long periods and so it is recommended that solutions be analysed as soon as possible after they are prepared.

Zinc has been deposited from alkaline solutions by a number of analysts, *e.g.* CLARKE AND HERMANCE[10]. The form of deposit from such solutions is often unsuitable for quantitative work because of its granular form and tendency to oxidize rapidly. The deposit may even be pyrophoric[11]. We have found that the best conditions for quantitative deposition of zinc in adherent form is from a buffered acetate solution at about pH 4.6 and that there is a slight advantage in employing a copper coated cathode.

METHOD FOR BRASSES AND BRONZES

The alloy is dissolved in an electrolysis tube in hydrochloric acid with addition of small quantities of potassium chlorate. The solution is then evaporated in a water-bath almost to dryness. One millilitre of concentrated hydrochloric acid and 5 drops of hydrazine hydrate solution (50%) are added and then water to cover the electrodes. The solution is heated to about 80° C in a water-bath, stirred with hydrogen or nitrogen and the applied voltage raised until deposition is proceeding at a satisfactory rate (0.8 V). The time of electrolysis depends on the amount of material and is about 20 minutes for quantities of 5-10 milligrams. The voltage is kept constant until the current has fallen to one tenth of its original value, then increased by about 0.05 V, and electrolysis continued until the current is about 3 milliamperes. Washing, separation and drying of the electrode is carried out as previously described[8] and the electrode is weighed. The copper coated cathode is replaced in the electrolyte at 40° C and electrolysis is continued at 1.3 to 1.4 V for 15 minutes. The vessel is then cooled by surrounding it with cold water, one drop of bromophenol blue indicator is added and then hydrazine hydrate until the solution is just blue. Washing, separation and drying then are effected as usual. Tin and lead are weighed together, but lead may be separately determined as dioxide after redissolving the mixed deposit, if desired. For determination of zinc in the residual electrolyte the hydroxide is precipitated with $2N$ sodium hydroxide and is then just redissolved with $2N$ acetic acid, the final pH being about 4.6. After heating to 40° C electrolysis is continued for 25 minutes at 1.25 V and, as no other metals have to be determined, the electrodes are washed by removing the electrolyte and replacing it with a vessel of distilled water. The cathode and deposit is dried and weighed as before.

Typical results for brasses and bronzes are shown in Tables I and II respectively.

TABLE I

RESULTS OF BRASS ANALYSIS

(a) The alloy used had the composition, copper 65.0, tin 1.37 lead 1.45 and zinc 31.9 per cent.

Wt. alloy used mg	Wt. Cu calculated mg	Wt. Cu obtained mg	Wt. Sn & Pb calculated mg	Wt. Sn & Pb obtained mg	Wt. Zn calculated mg	Wt. Zn obtained mg
16.54	10.75	10.73	0.46	0.44	4.27	4.28
12.20	7.93	7.94	0.34	0.33	3.89	3.87
16.82	10.93	10.93	0.47	0.46	5.37	5.34
15.36	9.98	9.98	0.43	0.43	4.90	4.88
13.98	9.09	9.07	0.39	0.35	4.46	4.45
17.95	11.67	11.68	0.50	0.48	5.73	5.74
11.58	7.53	7.50	0.33	0.33	3.69	3.70
14.23	9.25	9.24	0.40	0.39	4.54	4.53
16.12	10.48	10.40	0.45	0.47	5.14	5.15
14.63	9.51	9.50	0.41	0.39	4.66	4.66

(b) The alloy used had the composition, copper 67.71, tin 1.4, lead 0.7 and zinc 30.0 per cent.

Wt. alloy used mg	Wt. Cu calculated mg	Wt. Cu obtained mg	Wt. Sn & Pb calculated mg	Wt. Sn & Pb obtained mg	Wt. Zn calculated mg	Wt. Zn obtained mg
15.43	10.44	10.44	3.24	3.21	4.63	4.65
12.71	8.60	8.58	2.67	2.67	3.81	3.80
12.01	8.13	8.11	2.52	2.50	3.60	3.63
13.25	8.97	8.99	2.78	2.72	3.97	3.97
17.19	11.63	11.63	3.61	3.60	5.16	5.15
16.60	11.24	11.22	3.48	3.48	4.98	4.93

TABLE II

RESULTS OF BRONZE ANALYSIS

(a) The alloy used had the composition, copper 87.95, tin 9.22, lead 1.31 and zinc 1.37 per cent.

Wt. alloy used mg	Wt. Cu calculated mg	Wt. Cu obtained mg	Wt. Sn & Pb calculated mg	Wt. Sn & Pb obtained mg	Wt. Zn calculated mg	Wt. Zn obtained mg
9.10	8.01	9.01	0.94	0.91	0.13	0.14
5.81	5.12	5.14	0.60	0.62	0.08	0.08
6.20	5.45	5.43	0.64	0.64	0.08	0.09
9.67	8.51	8.51	0.99	0.99	0.13	0.14
6.62	5.82	5.81	0.68	0.68	0.09	0.07
6.65	5.85	5.85	0.69	0.67	0.09	0.09
7.22	6.35	6.34	0.75	0.76	0.10	0.08

(b) The alloy used had the composition, copper 87.1, tin 9.64, lead 0.40 and zinc 2.71 per cent.

Wt. alloy used mg	Wt. Cu calculated mg	Wt. Cu obtained mg	Wt. Sn & Pb calculated mg	Wt. Sn & Pb obtained mg	Wt. Zn calculated mg	Wt. Zn obtained mg
11.60	10.10	10.10	1.16	1.15	0.31	0.33
10.87	9.47	0.45	1.09	1.08	0.29	0.33
16.72	14.57	14.54	1.68	1.69	0.45	0.45
7.37	6.47	6.45	0.74	0.70	0.20	0.22
8.43	7.34	7.32	0.85	0.86	0.23	0.27
12.17	10.60	10.60	1.21	1.20	0.33	0.33

References p. 152.

It will be noted that micro-scale electrolytic analysis affords a rapid method of analysing small amounts of alloys such as might be available as a small paring from a specimen or object from which a larger sample may not be taken. The use of such a sample for analysis might well be criticised on account of the heterogeneous nature of some alloys, but in practice it has been demonstrated that errors are small and that alloy specimens having the same compositions are clearly recognizable. Complete analysis of these alloys may be effected in about 2 hours excluding the time necessary to bring the sample into solution.

The authors wish to acknowledge from Messrs. I.C.I., Limited, a grant which was used to purchase chemicals and consumable apparatus.

SUMMARY

The microchemical electrolytic analysis of alloys employing the methods of SAND AND LINDSEY for potential control have been extended to include complete analyses of brasses and bronzes in chloride solutions. The methods, employing from 5 to 20 milligrams of material, may be completed in about 2 hours (excluding the time necessary to bring the sample into solution) and are especially useful in circumstances where only a few milligrams of sample are available.

RÉSUMÉ

Les méthodes d'analyse électrolytique microchimique, pour les alliages, utilisant les procédés de SAND ET LINDSEY ont été appliquées, à l'analyse complète des laitons et des bronzes en solution chlorhydrique. Ces méthodes, utilisant 5 à 20 mg d'alliage, peuvent être effectuées en 2 heures environ (sans compter le temps nécessaire à la mise en solution de l'échantillon); elles sont particulièrement utiles lorsqu'on ne dispose que de quelques milligrammes d'échantillon.

ZUSAMMENFASSUNG

Die mikroelektrolytischen Analysenmethoden von Metallegierungen, die auf dem Prinzip von SAND UND LINDSEY beruhen, wurden auf die Gesamtanalysen von Messing und Bronze in salzsaurer Lösung angewendet. Diese Methoden, welche 5 bis 20 mg Legierung benötigen, können in ungefähr 2 Stunden ausgeführt werden (die Zeit für die Auflösung des Musters nicht gerechnet). Die Methoden sind besonders vorteilhaft, wenn man nur über einige Milligramme Substanz verfügt.

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THEORY OF PHOTOELECTRIC COMPLEX FORMATION TITRATIONS USING METAL INDICATORS

by

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Complex-formation titrations using metal indicators were introduced by SCHWARZENBACH[1], and in recent years these methods have acquired very great popularity among analysts.

The metal complexes formed by ethylendiaminetetra-acetic acid (EDTA) are particularly strong, and hence, when an equivalent amount of this reagent is added to the solution of a metal salt, the reaction proceeds for most metals practically to completion. If suitable metal indicators are available, these methods offer excellent possibilities for titrating various metals with an extraordinarily high degree of accuracy. Moreover, it seems possible to perform the titrations in extremely dilute solutions and hence to determine minute amounts of the metals. Such analyses, however, demand very sensitive methods for the detection of end-points; the photoelectric methods seem to be particularly suitable for the purpose.

The theory of photoelectric neutralizations using acid-base indicators was developed by RINGBOM AND SUNDMAN[2] in 1939. The considerations outlined in their paper can to a large extent be applied to complex-formation titrations. According to the acid-base concept of LEWIS, a complex-formation titration is actually a type of neutralization. Consequently, in the equations derived for pH measurements we have only to substitute pM (the negative logarithm of the metal ion concentration) for pH.

The sensitivity of a photometric pH measurement is defined by the equation

$$\frac{\text{pH-units}}{\text{transmittance, 1\%}} = \frac{\mathrm{dpH}}{\mathrm{d}I} = -\frac{(\log e)^2}{EI(1-\alpha)} = -\frac{0.188}{EI(1-\alpha)} \quad \ldots\ldots\ldots\ldots \quad (1)$$

where I is the percentage transmittance and E is the extinction (absorbance, optical density). Here it is assumed that the indicator is a one-colour indicator, only the alkaline form of which absorbs light; α is the fraction of the indicator appearing in the coloured form.

If a coloured indicator substance A reacts with a metal ion M to form a compound MA which does not absorb light of the wavelength used, the equation corresponding to Eq. 1 reads*.

$$\frac{\text{pM units}}{\text{transmittance, } 1\%} = \frac{\mathrm{dpM}}{\mathrm{d}I} = -\frac{0.188}{EI(1-\alpha)} = -\frac{0.188(1+K_{\mathrm{MA}}[\mathrm{M}])}{EI\,K_{\mathrm{MA}}\,[\mathrm{M}]} \quad \ldots \quad (2)$$

where K_{MA} is the stability constant of MA defined by

$$\frac{[\mathrm{MA}]}{[\mathrm{M}]\,[\mathrm{A}]} = K_{\mathrm{MA}} \quad \ldots \quad (3)$$

By means of Eq. 2 it is possible to calculate how sensitive an instrument is for changes in the metal ion concentration under various experimental conditions. It can easily be shown[2] that the sensitivity attains its maximum value when the indicator concentration corresponds to a transmittance value of 36.8%.

The theory of metal titrations with one-colour indicators will be elucidated below. However, most of the indicators in use have two colours, and hence the sensitivity of the instrument for changes in [M] is smaller than that given by Eq. 2. The expressions for two-colour indicators will be considered later.

Titrations with one-colour indicators

It seems appropriate to illustrate the theory of complex-formation titrations with titration curves analogous to those generally used in the theoretical treatment of neutralization reactions. As an example the titration curves referring to the reaction between EDTA and Cu^{+2} ions at various pH are given in Fig. 1. The curves are theoretical, and a possible precipitation of cupric hydroxide is not taken in consideration. The calculations are based on the following equilibrium constants determined by SCHWARZENBACH and co-workers:

Dissociation constants of EDTA = $\mathrm{H_4Y}$: $pk_1 = 2.0$; $pk_2 = 2.7$; $pk_3 = 6.2$; $pk_4 = 10.3$. $\log K_{\mathrm{CuY}} = 18.3$

It is important to know the metal ion concentration at the equivalence point. At this point

$$[\mathrm{M}]_{\mathrm{eq}} = [\mathrm{H_4Y}] + [\mathrm{H_3Y^{-}}] + [\mathrm{H_2Y^{-2}}] + [\mathrm{HY^{-3}}] + [\mathrm{Y^{-4}}] \quad \ldots \quad (4)$$

The fraction of the reagent not bound as a complex that appears as $\mathrm{Y^{-4}}$ will be denoted by β, *i.e.*

$$\beta = \frac{[\mathrm{Y^{-4}}]}{[\mathrm{H_4Y}] + [\mathrm{H_3Y^{-}}] + [\mathrm{H_2Y^{-2}}] + [\mathrm{HY^{-3}}] + [\mathrm{Y^{-4}}]} \quad \ldots \quad (5)$$

---

* Since no assumption is made about the charge of the indicator and the metal ion, the symbols are written without any sign of charge.

From the equations 3, 4, and 5, one obtains the general expression for the metal ion concentration at the equivalence point

$$[\mathrm{M}]_{\mathrm{eq}} = \sqrt{\frac{[\mathrm{MY}]_{\mathrm{eq}}}{\beta\ K_{\mathrm{MY}}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

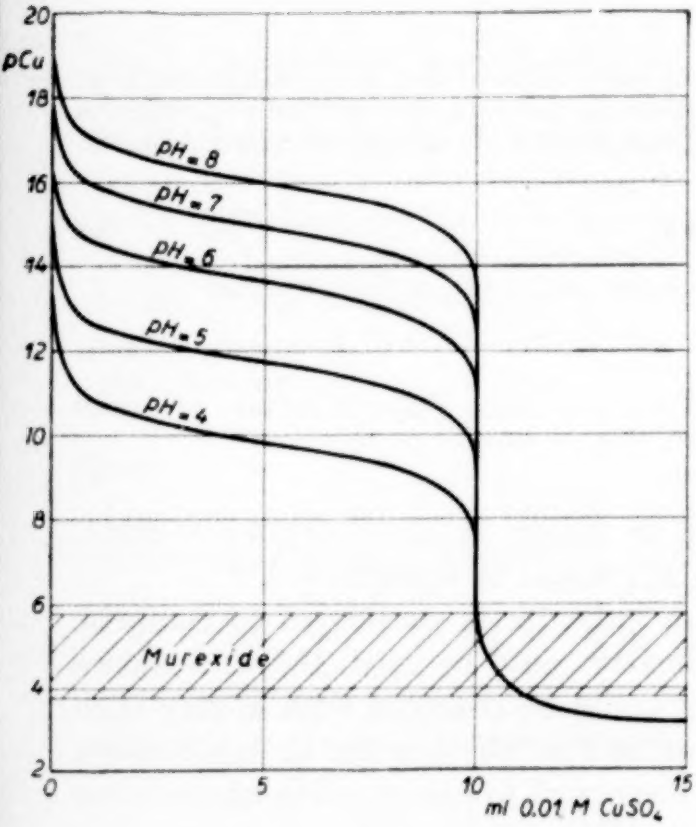

Fig. 1. Theoretical curves for the titration of 100 ml $10^{-3}M$ EDTA with $10^{-2}M$ $CuSO_4$ at various pH values.

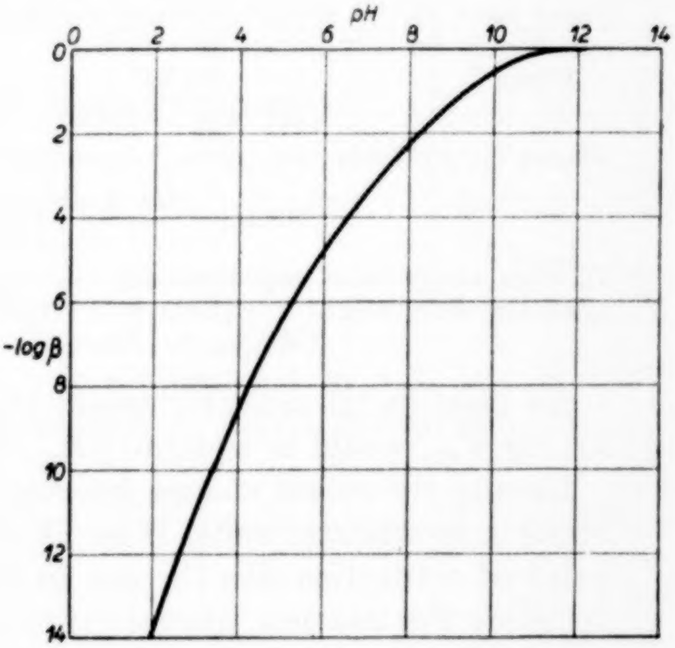

Fig. 2. The proportion of Y^{-4} ion at various pH values.

$$\frac{1}{\beta} = \frac{[\mathrm{H}^+]^4}{k_1\ k_2\ k_3\ k_4} + \frac{[\mathrm{H}^+]^3}{k_2\ k_3\ k_4} + \frac{[\mathrm{H}^+]^2}{k_3\ k_4} + \frac{[\mathrm{H}^+]}{k_4} + 1$$

β depends on the pH of the solution and can be calculated from the dissociation constants of EDTA. It is obtained in a simple way from the logarithmic plot given in Fig. 2.

If a metal indicator is used, it is of interest to know the exact value of the extinction at the equivalence point, *i.e.* E_{eq}. Assuming, as above, that the indicator A is coloured but MA is colourless, the extinction is proportional to [A]. On the other hand, if $E^{\max}$ denotes the extinction when no metal is present, $E^{\max} - E$ will be proportional to the concentration of MA formed. Consequently

$$\frac{E^{\max} - E}{[\mathrm{M}]\ E} = K_{\mathrm{MA}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

or

$$E_{eq} = \frac{E^{max}}{1 + K_{MA}\,[M]_{eq}} \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

When a complexing agent is titrated with a metal salt solution, E^{max} equals the extinction at the beginning, provided that the change in volume during the titration is neglected.

If the colour intensity of the indicator is not very high or if a very dilute solution is titrated, it will be necessary to pay attention to the fact that at the equivalence point part of the metal is bound to the indicator. The correction due to this error can easily be calculated as follows:

From

$$\frac{[MA]}{[M]\ (C_A - [MA])} = K_{MA} \quad (9)$$

where C_A denotes the total concentration of the indicator, it follows that

$$[MA]_{eq} = \frac{K_{MA}\ [M]_{eq}\ C_A}{1 + K_{MA}\ [M]_{eq}} \quad (10a)$$

In this expression representing the indicator correction, $[M]_{eq}$ is often so small that the denominator equals 1. In this case, Eq. 9 simplifies to

$$[MA]_{eq} \approx K_{MA}\ C_A\ [M]_{eq} \quad (10b)$$

An ideal metal indicator would change its colour at the equivalence point, *i.e.* log K_{MA} would be equal to pM_{eq}; then E_{eq} would be equal to $\frac{1}{2}$ E^{max}.

Usually the colour change interval of an indicator is considered to comprise about 2 logarithmic units. If an ideal indicator could be used, the equivalence point of a titration like the one in Fig. 1 could be detected with a very high accuracy. For instance, when titrating 100 ml of a $10^{-4}M$ solution at a pH above ca. 5 single drop of a $10^{-3}M$ titrant would be enough to pass over the whole colour change interval.

However, most known metal indicators do not form so strong complexes as EDTA and other similar complexing titrants. Hence it is often difficult to find an indicator that changes its colour near the equivalence point. For instance, murexide has been proposed as an indicator for the titration of copper with EDTA, but at pH values between 5 and 6 the stability constant of copper murexide is about $10^{4.8}$ (RINGBOM, SIITONEN AND VÄNNINEN[3]). The colour change occurs when pCu $\sim$ 4.8 whereas at the equivalence point pCu is about 7 to 8. Therefore, if EDTA is titrated with copper sulphate, the colour change will occur too late, as shown in Fig. 1.

If, however, a sensitive photoelectric instrument is used, even very small changes in pM can be detected. In other words, the photoelectric colour change interval of the indicator is much wider than two pM units. There is no difficulty in getting a deflection in the steep part of the curve close to the equivalence point, and the end-point of the titration will therefore appear as a very distinct break in the curve. This is shown in Fig. 3, where E_A, *i.e.* the extinction of the pure indicator, is plotted as a function of the volume of the added copper solution.

The exact pM value at the break-point can be calculated as follows:

For the change in the extinction $-\triangle E_A = E_A^{\max} - E_A$ close to $E_A^{\max}$ one obtains from Eq. 7:

$$-\frac{\triangle E_A}{E_A} = K_{MA}\,[M] \quad \text{. . . . .} \quad (11)$$

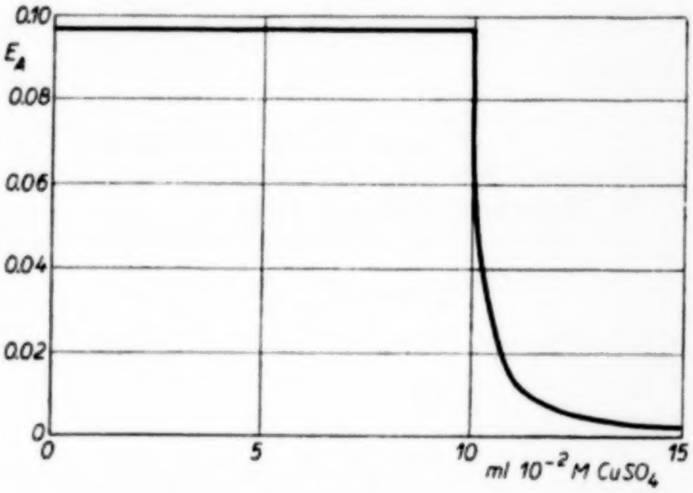

Fig. 3. Theoretically calculated change in E_A when titrating 100 ml $10^{-3}M$ EDTA with $10^{-2}M$ $CuSO_4$ at pH > 4 using murexide as indicator. $K_{CuA} = 10^{4.8}$, $E_A^{\max} = 0.0969$ ($I_A = 80\%$). No consideration is taken of the extinction owing to the colours of CuY^{-2}, Cu^{+2} and CuA nor of the dilution during the titration.

The galvanometer deflection is, however, not proportional to $\triangle E_A$ but to the change in the light intensity $\triangle I$. Differentiation of Beer's law gives

$$\triangle E_A = -\frac{1}{2.3} \cdot \frac{\Delta I}{I} \quad \text{. . . . .} \quad (12)$$

From Eqs. 11 and 12 one obtains

$$[M] = \frac{1}{2.3\,K_{MA}\,E_A}\,\frac{\triangle I}{I} \quad \text{. . . . .} \quad (13)$$

or

$$pM = \log 2.3\,K_{MA}\,E_A\,I - \log \triangle I \quad \text{. . . . . . .} \quad (14)$$

Usually the maximum sensitivity of a photoelectric instrument can be expressed in scale units per 1% transmittance (RINGBOM AND ÖSTERHOLM[4]). This sensitivity, which of course depends on the intensity and on the spectral composition of the light used (and in some degree also on the state of the photocell), is denoted by k_λ scale units/transmittance, 1%. A change in deflection of n scale units corresponds therefore to n/k_λ % transmittance. Hence

$$pM = \log 2.3\,K_{MA}\,E_A\,I\,k_\lambda - \log n \quad \text{. . . . .} \quad (15)$$

where n is the number of scale units when the maximum point of the curve is taken as zero.

This equation refers to the change in the photocurrent near the break-point of the curve, where E_A is not much less than $E_A{}^{\max}$. In Eq. 15 E_A can therefore

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be substituted by $E_A{}^{max}$. In other words, the relationship between pM and n is

$$\mathrm{pM} = \log 2.3\, K_{MA}\, E_A{}^{max}\, I\, k\lambda - \log n \quad \ldots\ldots\ldots \quad (16)$$

All the quantities on the right side of this equation are known or can easily be measured.*

If only whole scale units are taken in consideration, the drop in the curve starts at approximately $n = 1$. The pM value at this point is therefore approximately

$$\mathrm{pM}_{break} \approx \log 2.3\, K_{MA}\, E_A{}^{max}\, I\, k\lambda \quad \ldots\ldots\ldots \quad (17)$$

It therefore follows that

$$\mathrm{pM} \approx \mathrm{pM}_{break} - \log n \quad \ldots\ldots\ldots \quad (18a)$$

or

$$n \approx \frac{[\mathrm{M}]}{[\mathrm{M}]_{break}} \quad \ldots\ldots\ldots \quad (18b)$$

The assumption that $\mathrm{pM}_{break} \approx \mathrm{pM}_{n=1}$ is not justified if $\mathrm{pM}_{n=1}$ is considerably larger than pM_{eq}. In other words, $\mathrm{pM}_{n=1}$ must be on the steep part of the curve in Fig. 1.

The above considerations refer to the case where the indicator itself is coloured, but MA has no colour. If the compound MA is coloured and A is colourless, the equations given would require slight alterations: $(1-a)$ in Eqs. 1 and 2 would be replaced by a; in the other equations K_{MA} [M] would be replaced by $\frac{1}{K_{MA}[\mathrm{M}]}$

Titrations with two-colour indicators

Most metal indicators have two colours, *i.e.* MA as well as A absorb light. Using light of suitable wavelength it is possible to diminish an undesirable absorption, but it is difficult to eliminate such an absorption entirely. Consequently, the photometer will not indicate E_A — as was assumed in the previous section — but $E_A + E_{MA}$.

From Beer's law it follows that

$$\frac{E_{MA}}{E_A{}^{max} - E_A} = \frac{a_{MA}}{a_A} \quad \ldots\ldots\ldots \quad (19)$$

---

* If the indicator is the only coloured substance in the solution, I is the transmittance corresponding to $E_A{}^{max}$. But if other coloured substances are formed (*e.g.* when titrating with copper solutions) I is the transmittance of the solution at the equivalence point.

where a_{MA} and a_{A} denote the extinction coefficients (absorbance index) of the two species. In the following, the quotient $\frac{a_{\mathrm{MA}}}{a_{\mathrm{A}}}$ is denoted by γ. The value of γ is determined in the simplest way by measuring the extinction of a very dilute indicator solution first without any metals and then (at the same indicator concentration) with an excess of metal ions. If Beer's law is valid

$$\gamma = \frac{E_{\mathrm{MA}}^{\max}}{E_{\mathrm{A}}^{\max}} \quad \ldots \quad (20)$$

When a complexing agent is titrated with a metal salt solution, the extinction at the beginning is $E_{\mathrm{A}}^{\max}$, and the extinction measured at any point of the curve will be

$$E = E_{\mathrm{A}} + E_{\mathrm{MA}} = E_{\mathrm{A}} + \gamma\,(E_{\mathrm{A}}^{\max} - E_{\mathrm{A}}) \quad \ldots \quad (21)$$

From Eq. 7 it follows that

$$E_{\mathrm{A}} = \frac{E_{\mathrm{A}}^{\max}}{1 + K_{\mathrm{MA}}\,[\mathrm{M}]} \quad \ldots \quad (22)$$

and consequently from Eqs. 21 and 22 that

$$E = E_{\mathrm{A}}^{\max} \left\{\frac{1 + \gamma\, K_{\mathrm{MA}}\,[\mathrm{M}]}{1 + K_{\mathrm{MA}}\,[\mathrm{M}]}\right\} \quad \ldots \quad (23)$$

This equation makes it possible to calculate exactly the extinction at the equivalence point when a two-colour indicator is used. The value of $[\mathrm{M}]_{\mathrm{eq}}$ is computed from Eq. 6, and the corresponding extinction

$$E_{\mathrm{eq}} = E_{\mathrm{A}}^{\max} \left\{\frac{1 + \gamma\, K_{\mathrm{MA}}\,[\mathrm{M}]_{\mathrm{eq}}}{1 + K_{\mathrm{MA}}\,[\mathrm{M}]_{\mathrm{eq}}}\right\} \quad \ldots \quad (24)$$

γ depends of course on the light used; $E_{\mathrm{A}}^{\max}$ depends on the concentration of the indicator and on the thickness of the absorbing layer, and can be chosen at will.

In the previous section relating to the use of a one-colour indicator, Eqs. 14 to 18 were derived for titrations where the equivalence point was not within the (conventional) colour change interval of the indicator. For two-colour indicators the change in deflection will be smaller, and the quotient γ must be taken into consideration. It can easily be shown from Eqs. 19 and 21 that in this case

$$\triangle E = (1-\gamma)\triangle E_{\mathrm{A}} \quad \ldots \quad (25)$$

and Eqs. 14 and 17 will be changed into

$$\mathrm{pM} = \log 2.3\, K_{\mathrm{MA}}\, E_{\mathrm{A}}\, I\, (1-\gamma) - \log \triangle I \quad \ldots \quad (26)$$

and

$$\mathrm{pM}_{\text{break}} = \log 2.3\, K_{\mathrm{MA}}\, E_{\mathrm{A}}^{\max}\, I\, k_\lambda\, (1-\gamma) \quad \ldots\ldots\ldots \quad (27)$$

Examples of the use of the above equations will be given in the last section of this paper.

The dependence on Beer's law

All calculations made above are based on Beer's law. The light of filter photometers suitable for titrations is, however, usually far from monochromatic, and hence the law is valid only at low extinction values, *i.e.* at small indicator concentrations. For high extinctions an exact theoretical treatment is difficult. A treatment is nevertheless possible. For instance, a graphic method can be used: the absorption (or transmittance) of the indicator is plotted as a function of the logarithm of the concentration of the indicator. Such calculations have previously been made for pH measurements by means of acid-base indicators[2], and analogous considerations are possible when metal ion concentrations are measured with metal indicators.

Details will, however, not be given here. The general principle is that if Beer's law is not valid, the differentials needed must be determined experimentally[4].

The influence of acidity on complex-formation titrations

The acidity affects complex-formation titrations in two ways since the equilibrium state of the complex compound formed as well as the equilibrium state of the metal indicator depends on the acidity.

In Fig. 4 a curve taken from a paper by RINGBOM AND SANDÅS[6] is shown which

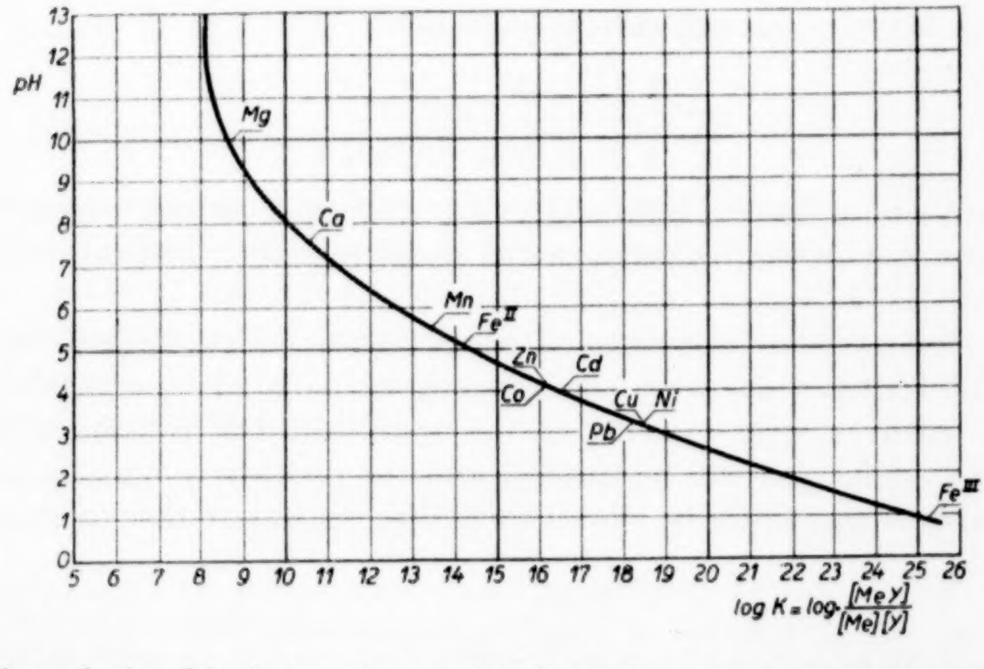

Fig. 4. The relationship between permitted acidity and complexity constant for the titration of various metals with EDTA.

illustrates the effect first mentioned when titrating various metals with EDTA. The stability constant K_{MY} is plotted as abscissa; the ordinate indicates the pH value where a concentration of the reagent of $10^{-5}M$ (*i.e.* $[H_4Y] + [H_3Y^-] + [H_2Y^{-2}] + [HY^{-3}] + [Y^{-4}] = 10^{-5}$) is sufficient to convert 99.9% of the metal into the complex MY (*i.e.* $\frac{[MY]}{[M]} = 1000$).

If pH is larger than the value corresponding to pK_{MY}, the formation of Y ions and hence of MY will be favoured, presuming, of course, that no formation of hydroxocomplexes or hydroxides occurs. The latter reactions are the reason why in titrating many metals (*e.g.* Fe, Cu, Zn, Mg) there is a limiting value of pH also on the alkaline side.

The acidity usually influences the colour change of the metal indicator since, as a rule, the indicator splits off one or more hydrogen ions. The equilibrium situation will then be rather involved. SCHWARZENBACH[5] has for practical purposes suggested the use of the constant $\frac{[MA]}{[M][A]} = K_{MA}$, where [A] denotes the concentration of the various species of the free indicator, whereas [MA] is the concentration of the indicator bound to the metal. In this way the mathematical relationship will be rather simple, but the "constant" K_{MA} will change with the acidity. For instance, the stability constant of calcium murexide increases considerably with increasing pH in alkaline solutions.

The use of comparison solutions

Comparison solutions can sometimes be useful in complex-formation titrations. In order to take full advantage of the sensitivity of the photoelectric methods, it is desirable that the composition of the comparison solution is exactly the same as the composition of the unknown solution at the equivalence point. The problem of preparing such a solution seems at first sight impossible to solve. However, there is an astonishingly simple way to do this, as was shown by RINGBOM AND SUNDMAN[2]. These authors recommended the following procedure for acid-base titrations:

A comparison solution is prepared that contains the reaction product (or the reaction products) of the titration at exactly the same molarity as the concentration of the titrant; furthermore, the reaction product is added to the sample solution before the titration to give a concentration also equal to the concentration of the titrant.

Hence, if a metal M is to be titrated with $0.01M$ EDTA solution, the comparison solution should contain exactly 0.01 mole of MY per liter; moreover MY should be added to the sample solution until this solution also contains 0.01 mole of MY per liter. The content of buffer substances (*i.e.* the pH value) and the indicator concentration must, of course, be exactly the same in the two solutions.

The addition of the reaction product to the sample solution will diminish the sharpness of pM-jump. However, this fact is of little importance when the end-point of the titration is indicated with a photoelectric method that is sensitive to pM changes of ±0.01 units or less. It is more important that at the equivalence point the sample solution has exactly the same composition as the comparison solution.

It may be noted that as long as the concentration of the titrant is not altered, the same comparison solution can always be used. The method described avoids any calculations of titration errors.

The use of comparison solutions is advantageous when the pM jump is not very large and when a suitable indicator is available. For many complex-formation titrations with EDTA, the break in the titration curve is, however, so sharp that a comparison solution is not necessary.

The accuracy of photoelectric complex-formation titrations

It is clear from the previous considerations that the precision as well as the accuracy of photoelectric complex-formation titrations is extremely high. If, in the titration of copper with $10^{-2}M$ EDTA (Fig. 1), the equivalence point is determined with a precision of, say, ±0.5 pCu, the corresponding error when pH = 5 will be about ±0.01%; if the pH is higher, the theoretical error will be still smaller. Using murexide as indicator, the break-point of a curve like the one in Fig. 3 can theoretically be detected with almost this degree of precision. If an indicator could be found that changes colour close to the equivalence point (pCu = 7 — 8), very accurate titrations in concentrations of $10^{-5}M$ or still less should be possible, although many trivial sources of error must then be considered (purity of the reagents, adsorption at surfaces etc.).

When comparison solutions are used, the detection of the end-point is usually so precise that other factors determine the accuracy attainable.

Procedures in the literature often prescribe titrations in ammonia buffer solutions (*e.g.* Zn, Cu, Ni, Cd), since metal hydroxides will otherwise precipitate. It may be noted that the formation of metal ammine complexes will affect the shape of the titration curves: the jump will be considerably less steep. Nevertheless the precision is sufficient for most determinations in practice. If a high degree of accuracy is required or if very dilute solutions are titrated, it may be advantageous, however, to buffer the solution with substances that do not form any strong complexes with the metal in question, *e.g.* with bicarbonate. In order to avoid any precipitation of metal hydroxides before the equivalence point, the use of the metal salt solution as the titrant is recommended, as in the experiments of the present study.

EXPERIMENTAL

A Lange two-cell filter photometer was used in the experiments carried out in order to test the theoretical predictions of the accuracy of the titrations. The deflection of the galvanometer was proportional to the absorption of the solution. The maximum sensitivity of the instrument was $4.5 \cdot 10^{-9}$A per scale unit.

At first some titrations will be described where pM_{eq} is considerably larger than $\log K_{MA}$. Figs. 5 and 6 illustrate the titration of 100 ml 10^{-3} *M* Na_2H_2Y with 10^{-2} *M* $CuSO_4$ solution using murexide as indicator. In Fig. 5 the extinction is plotted as a function of the added volume of $CuSO_4$. Fig. 6 shows the photocurrent close to the equivalence point using the maximum galvanometer sensitivity. If the galvanometer needle approached the end of the scale (= 200 scale units), it was readjusted to zero by balancing the photocurrent by means of an iris diaphragm.

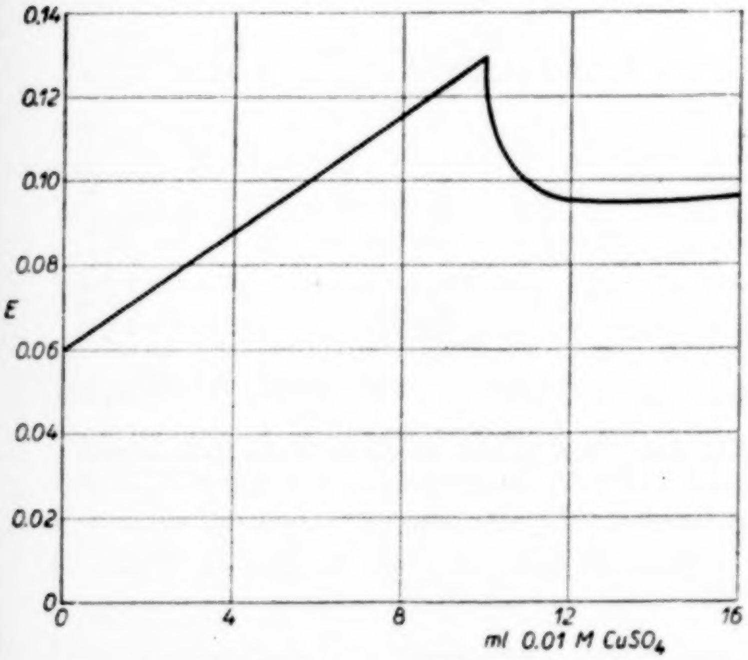

Fig. 5. Experimentally determined change in extinction when titrating 100 ml of 10^{-3}*M* EDTA with 10^{-2}*M* $CuSO_4$ at pH = 5.5 ($NaHCO_3$-H_2CO_3 buffer) using murexide as indicator. Light blue filters.

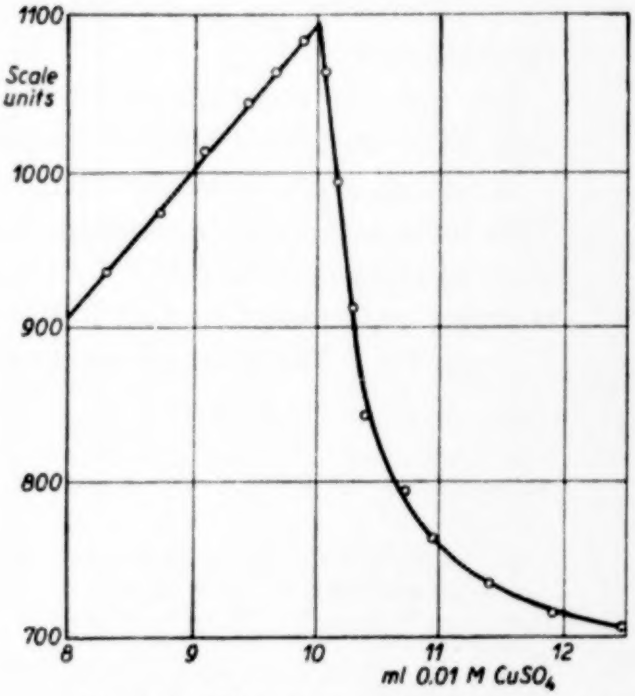

Fig. 6. The same titration as in Fig. 5 close to the equivalence point using maximum sensitivity of the galvanometer.

The deep blue colour of the CuY^{-2} ions causes a continuous rise in the curve before the equivalence point. After this point, the colour of the Cu^{+2} ions slightly affects the extinction values, but this effect is very small. It may be noted that the precision of the titration is increased by the rise before the equivalence point since a sharp angle is advantageous for detecting the end-point.

The value of pCu at the break-point and the shape of the curve after this point can be calculated by means of the Eqs. 27 and 18. In other words

$$pCu = \log 2.3\, K_{CuA}\, E_{A}^{\max}\, I\, k_{\lambda}\, (1-\gamma) - \log n \quad \ldots\ldots \quad (28)$$

where the first term on the right side denotes pCu_{break}, and n is the number of scale units after the maximum point. K_{CuA} is $10^{4.83}$. In the experiment of Fig. 6, E_A^{max} was 0.055 corresponding to $I_A = 88.1\%$, but owing to the blue colour of CuY at the equivalence point a smaller value of $I = 74.3$ must be used; k_λ was 83 scale units per 1% transmittance when a 15 watt lamp and light blue filters were used; for γ, calculated from Eq. 20, the value 0.86 was obtained. Consequently, pCu_{break} is 6.87, or

$$pCu = 6.87 - \log n \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (29)$$

The value of pCu at the equivalence point calculated from Eq. 6 is 7.8, and hence the break occurs a little too late. The difference between the consumption of the titrant between the two points is, however, too small to cause any noticeable titration error.

The value of n calculated from Eq. 29 and from the curve of Fig. 1 agree very well with the experimental values of Fig. 6.

A change in the indicator concentration slightly affects the value of pCu_{break}. This term attains its maximum value, *i.e.* the indicator is most sensitive for M ions, when the product $E_A^{max}\,I$ has its maximum. (If the metal ion and the MY complex are colourless and if Beer's law is valid, the maximum is attained at $I = 36.8\%$.) The shift of the break-point with varying indicator concentration

TABLE I

TITRATIONS OF EDTA WITH $0.01\,M$ $CuSO_4$ SOLUTION USING MUREXIDE AS INDICATOR

g Na_2H_2Y sol. containing $9.775 \cdot 10^{-2}$ mmol/g	pH (NH_4Ac-HAc buffer)	ml $0.01\,M$ $CuSO_4$ consumed theor.	obtained	% error
4.7423	5.4	46.355	46.36	+0.01
4.5770	5.4	44.74	44.74	±0
4.6007	5.4	44.97	44.99	+0.04
4.6461	5.4	45.415	45.40	—0.03
4.7170	5.4	46.11	46.11	±0

TABLE II

TITRATIONS OF EDTA WITH $0.001\,M$ $CuSO_4$ SOLUTION USING MUREXIDE AS INDICATOR

g Na_2H_2Y sol. containing $7.954 \cdot 10^{-3}$ mmol/g	pH ($NaHCO_3$-H_2CO_3 buffer)	ml $0.001\,M$ $CuSO_4$ consumed theor.	obtained	% error
5.2069	6.2	41.41	41.30	—0.26
4.9534	6.2	39.40	39.55	+0.38
5.0310	6.2	40.02	40.05	+0.07
5.0603	6.2	40.25	40.10	—0.38
4.9304	6.2	39.21	39.27	+0.15

is not as a rule very large, at most a few tenths of a pM unit. In a more effective way it is possible to change pM_{break} by altering k_λ through adjustment of the sensitivity of the galvanometer or the intensity of the light.

In Tables I and II the results of some titrations of EDTA with $10^{-2}M$ and $10^{-3}M$ $CuSO_4$ solutions are given.

When a $10^{-2}M$ solution was used as titrant, the error was below ±0.04%. When a $10^{-3}M$ solution was used, the percentage error was a few tenths. The break of the curve in Fig. 7 showing a titration with $10^{-3}M$ solution is still rather sharp.

The amount of EDTA solution was weighed by means of a weighing burette; for the titration an accurately calibrated chamber burette[7] was used in order to diminish the error of reading.

In order to investigate titrations where pM_{eq} was near the middle of the colour change interval some determinations of magnesium using Eriochrome black T were performed. The pH of the solution was about 10, and according to SCHWARZENBACH at this acidity log K_{MgA} is 5.5. Log K_{MgY} is 8.7. If the total concentration of magnesium is between 10^{-2} and 10^{-3}, the corresponding pM_{eq} value calculated from Eq. 6 is between 5.1 and 5.6. The point of colour change is thus not far from the equivalence point. The exact value of the extinction at the equivalence point can be calculated from Eq. 24, *i.e.*

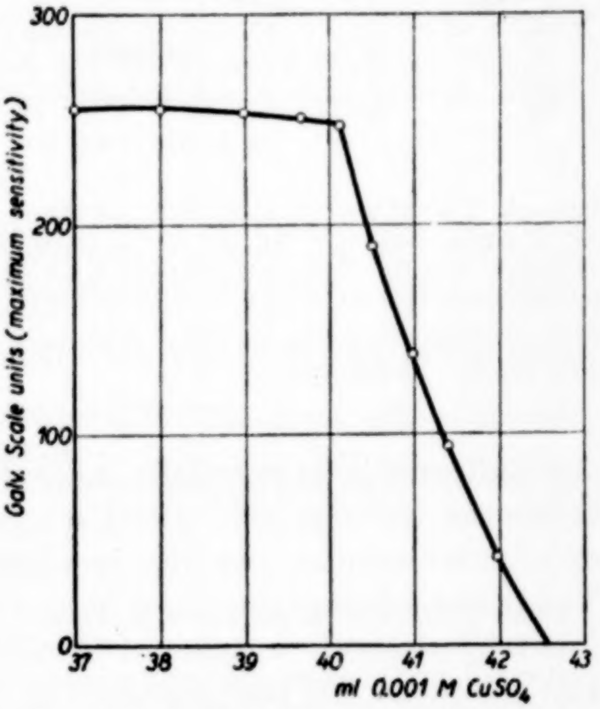

Fig. 7. Experimentally determined change in photocurrent when titrating 100 ml $10^{-4}M$ EDTA with $10^{-3}M$ $CuSO_4$ at pH = 6.2 ($NaHCO_3$-H_2CO_3 buffer) using murexide as indicator.

$$E_{eq} = E_A^{max} \left\{ \frac{1 + \gamma K_{MA}[M]_{eq}}{1 + K_{MA}[M]_{eq}} \right\} \quad \ldots\ldots\ldots\ldots\ldots \quad (24)$$

When red filters were used γ was 0.54. Consequently $E_{eq} = 0.67 E_A^{max}$ for $[MgY^{-2}] = 0.01$.

The sharpness of the detection of the equivalence point will be clear from Fig. 8 illustrating the change of E near the equivalence point when titrating with *ca.* $0.02M$ Na_2H_2Y solution. If a very accurate value of E_{eq} is required, attention must be paid to the change of the acidity during the titration.

In this way the molarity of the approximately $0.02M$ Na_2H_2Y solution was determined from weighed samples of a $MgSO_4$ solution. The precision attained in a series of titrations was about ±0.04%.

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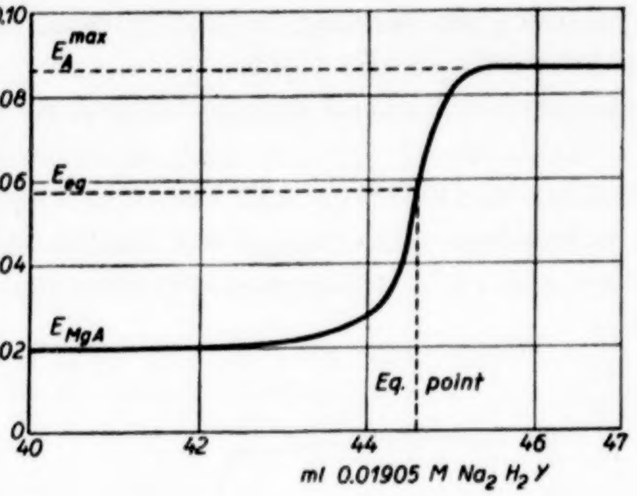

Fig. 8. Titration of a $MgSO_4$ solution with *ca.* 0.02*M* Na_2H_2Y at pH = 10 using Eriochrome black T as indicator. Red filters, volume at the eq. point = 100 ml. Theoretical consumption: 44.60 ml. Obtained consumption: 44.60 ml.

Table III shows the results of some determinations of magnesium using a comparison solution prepared according to the directions given in a previous section. A cuvette was filled with the comparison solution, the indicator was added, and the photocurrent was balanced by means of the iris diaphragm of the instrument until the galvanometer needle was at the middle of the scale. The comparison solution was then replaced by the unknown and titrated with a 0.005*M* Na_2H_2Y solution until the same deflection value was reached at the same galvanometer sensitivity. Buffer solution, magnesium complex, and indicator in appropriate concentrations were added to the sample solution before the titration. The solution thus contained 0.005 moles MgY^{-2} and 50 ml of a buffer solution per liter in addition to the unknown amount of magnesium. The buffer solution contained 350 ml 25% NH_3 + 54 g NH_4Cl per liter. 1.50 ml of a 0.01% alcoholic solution of Eriochrome black T per 100 ml were added to the two solutions. The transmittance of the standard solution was about 85%.

Near the equivalence point an amount of indicator corresponding to the consumed volume of the titrant was added. The volume of the indicator added must be very carefully measured. If the approximate consumption of titrant is known before the titration all the indicator can be added at the beginning.

TABLE III

TITRATIONS OF $MgSO_4$ SOLUTIONS WITH EDTA USING A COMPARISON SOLUTION CONTAINING 0.005 MOLES MgY^{-2} + 50 ml BUFFER SOLUTION PER LITER

g $MgSO_4$ solution containing 0.09903 mmol/g	ml 0.005*M* Na_2H_2Y consumed	mg Mg		% error
		theor.	obtained	
2.3295	46.14	5.610	5.611	+0.02
2.2349	44.25	5.382	5.381	—0.02
2.2778	45.07	5.485	5.481	—0.07
2.3019	45.49	5.544	5.532	—0.22
2.3501	46.64	5.660	5.671	+0.20
2.3170	45.92	5.580	5.584	+0.07
2.3191	45.90	5.585	5.581	—0.07

The change of the photocurrent close to the equivalence point was about

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20 scale units per 0.02 ml of the 0.005M titrant. Considering that only about 5 mg of magnesium are titrated, the accuracy is very satisfactory. It is likely that the errors would be further diminished, if the temperature were kept strictly constant.

SUMMARY

The general principles of photoelectric complex formation titrations using metal indicators are given and the mathematical equations necessary for the exact determination of the equivalence point are derived for titrations with one-colour and two-colour indicators.

A method for preparing a comparison solution of exactly the right composition is suggested.

The influence of various factors on the titrations is discussed and it is shown that the theoretically attainable precision and accuracy are extremely high.

Some titrations of copper and magnesium with EDTA are described which illustrate the accuracy attainable.

RÉSUMÉ

On examine les principes généraux des titrages photoélectriques par formation de complexes, en employant des indicateurs pour ions métalliques. On dérive les formules mathématiques nécessaires pour la détermination exacte du point d'équivalence, avec deux types d'indicateurs.

On propose un nouvelle méthode pour la préparation d'une solution de référence du complexe formé.

On discute l'influence de différents facteurs sur les déterminations, et l'on montre que la précision théorique est extrêmement grande.

On décrit quelques titrages de cuivre et de magnésium par EDTA pour démontrer le degré de précision qu'on peut atteindre.

ZUSAMMENFASSUNG

Es wurde die Theorie der photoelektrischen Komplexbildungstitrationen unter Verwendung von Metallindikatoren entwickelt, auch wurden mathematische Ausdrücke für die exakte Bestimmung des Äquivalenzpunktes abgeleitet. Die Berechnungen sind sowohl für einfarbige Indikatoren als für zweifarbige Indikatoren durchgeführt.

Eine Methode für die Bereitung einer Vergleichslösung mit genau dem richtigen Gehalt an Komplexsalt wurde vorgeschlagen.

Der Einfluss verschiedener Faktoren auf die Titrationen wurde erörtert, und es wurde gezeigt dass die theoretisch erreichbare Genauigkeit und Präzision ausserordentlich hoch sind.

Einige Titrationen von Kupfer und Magnesium wurden beschrieben, welche die in Praxis erreichbare Genauigkeit veranschaulichen.

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COLORIMETRIC DETERMINATION OF IRON WITH MECONIC ACID

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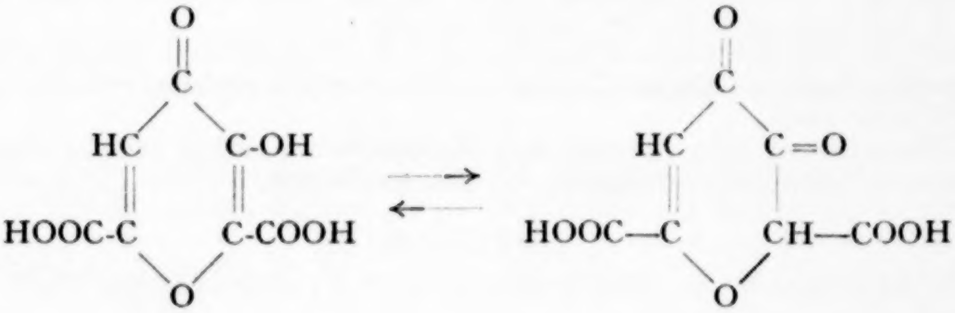
DER WIELEN[1] has studied the determination of meconic acid in opium and he proposed the use of the colorimetric reaction with iron chloride for this purpose: afterwards WOINOFF[2] suggested the employment of meconic acid for the determination of vanadium ion. WELCHER[3], then, in his book *"Organic Analytical Reagents"* regards this acid as suitable as reagent for the ferric ion because it reacts with ferric chloride in the presence of hydrochloric acid to give a red colour.

The object of this paper is to investigate the use of meconic acid as a colour-forming complex and to study its application to the colorimetric determination of the ferric ions.

Meconic acid is a substance obtained from opium and consists of white crystals. It is slightly soluble in cold water, in about five parts of boiling water and is soluble in alcohol and benzene. Its structural formulas are:



Apparatus and reagents

In the present investigation a Beckman Model DU Spectrophotometer was used. The absorption cells were of Corex with 1.00 cm path length.

Iron chloride and meconic acid analytical grade were used in the preparation of standard solutions.

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Spectrophotometric study of colour reaction

To determine the complex present, JOB's method of continuous variations[4] and a method employing spectrophotometric titrations[5] were applied.

JOB's method consists in noting the difference in optical density of a system while varying the mole fraction of components, and the coordination number of the central atom is found by applying this formula:

$$N = \frac{a}{1 - a}$$

where a is the mole fraction of complexing ion present at maximum difference in optical density.

In the second method a number of solutions are prepared containing the same concentration of the central atom and the complexer in amounts ranging from 0 to n times the concentration of central atom. The coordination combinations are determined from breaks in the slope of the curve of optical density.

Fig. 1 shows the complexation using JOB's method and it is clearly indicated that a compound exists containing one atom of iron and one meconic acid residue.

Fig. 2 shows the results of spectrophotometric titrations and experiments gave a definite break at ratio 1:1 which confirmed the result of JOB's method.

The study of the red complex with ionophoresis shows that this complex is fundamentally neutral.

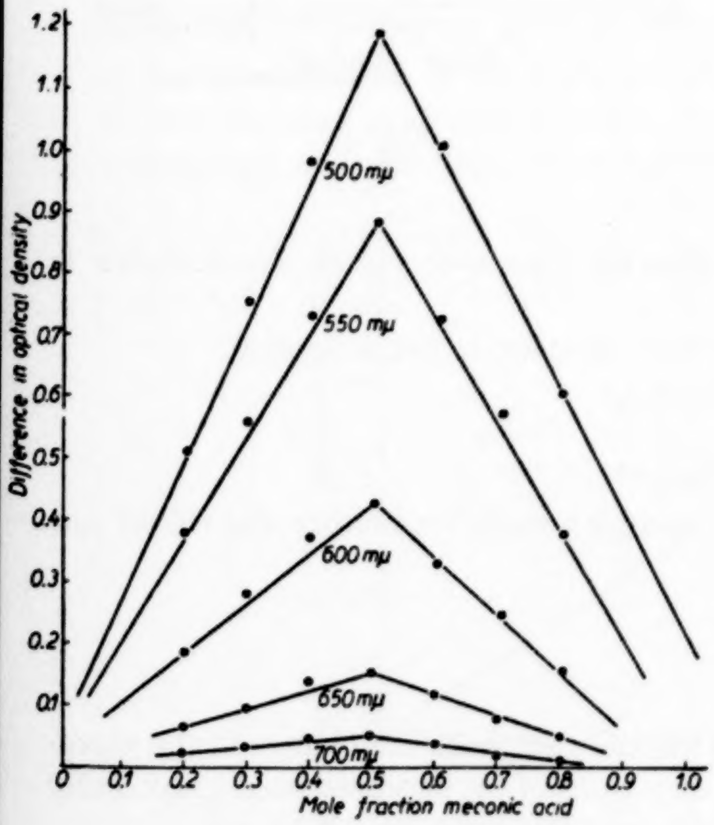

Fig. 1

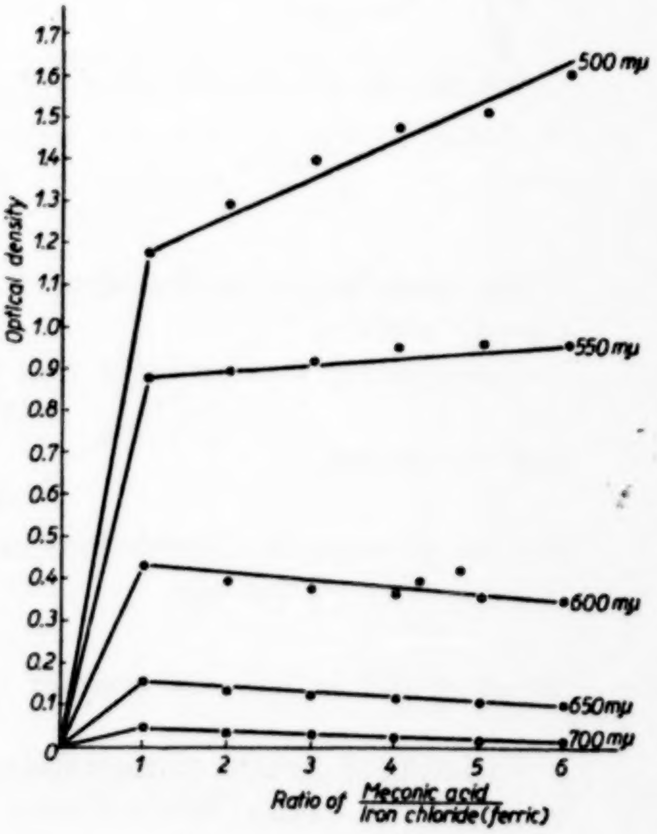

Fig. 2

References p. 172.

With the aim of obtaining a thorough knowledge of this ion, because the chloride ion is a complexing one itself, we have executed the same investigations replacing the chloride ion with the perchloric ions. This new complex is also red and its behaviour is analogous to the first complex.

Fig. 3 shows the spectrophotometric curves of both complexes and Fig. 4 the results of the spectrophotometric titrations for the second complex.

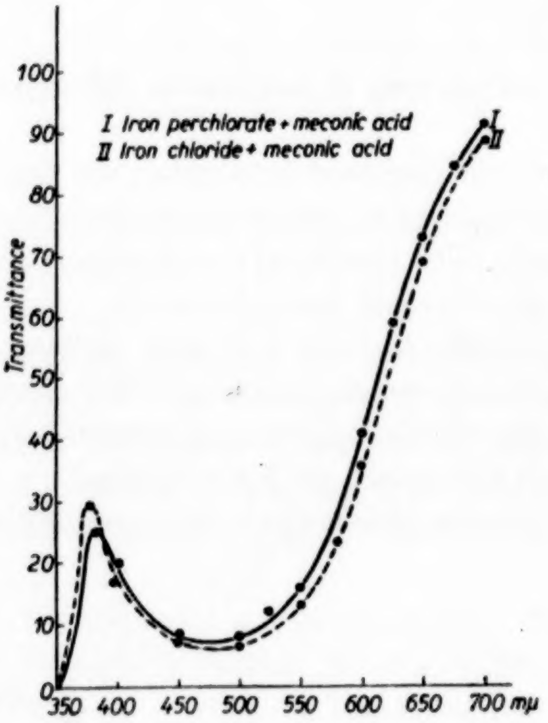

Fig. 3

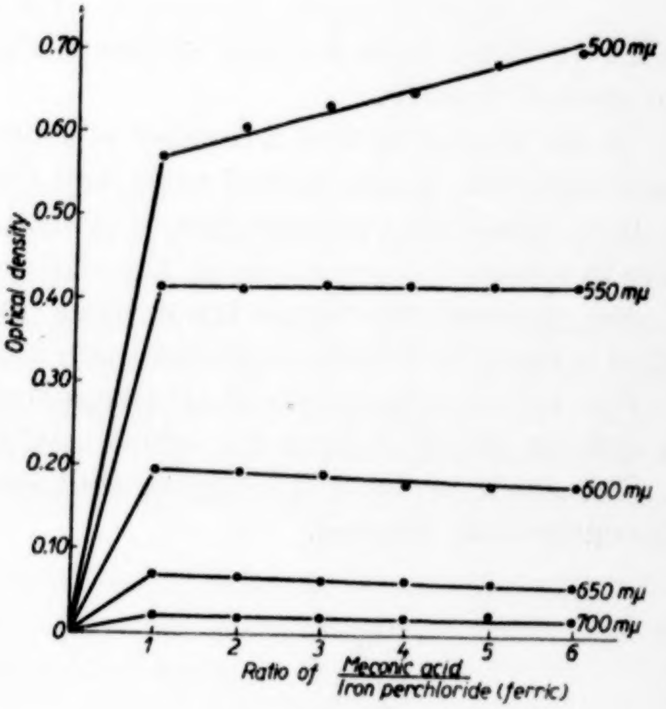

Fig. 4

The ionophoresis in the absence of chloride ions shows that the complex is sharply positive.

Consequently it is probable that the first complex is the following:

$$[Fe(Mec)Cl_2]$$

and the second:

$$Fe(Mec)^{+2}$$

but the presence of chloride ions in the complex modifies neither the colour nor the intensity of this one.

Effect of pH on coloured complex

Variation of pH affects the stability of the red complex. The change in the wavelength of the maxima of absorbency to variations of pH is represented graphically in Fig. 5: the red complex is stable in the range of pH from 0.8 to 3.6.

References p. 172.

Beer's law applied to iron complex

Beer's law is valid for the red complex at low pH values. With solutions at pH = 1 we have obtained quite satisfactory results. Fig. 6 shows the curve at 475 mμ with amounts of iron ranging from 0 to 30 micrograms for ml. The measurements are made using 0.5 to 11 ml of solution of Fe^{+3} $1 \cdot 10^{-3}M$ adding 2 ml of HCl $2N$, 5 ml of solution of meconic acid $1 \cdot 10^{-2}M$ and diluting to a total volume of 20 ml.

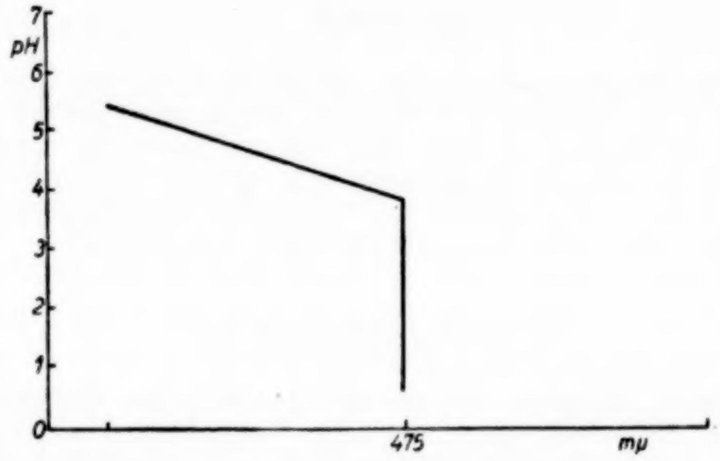

Fig. 5

Sensitivity of reaction

The limit of the red complex is the detection of one part of iron in 5,000,000 parts of solution when observation is made in a 50-cm tall form Nessler's cylinder.

Spot-plate sensitivity

An investigation of the limit of identification and the limiting concentration of the meconic acid test for iron shows that the limit of identification is 0.5 microgram at a limiting concentration of 1 : 400,000.

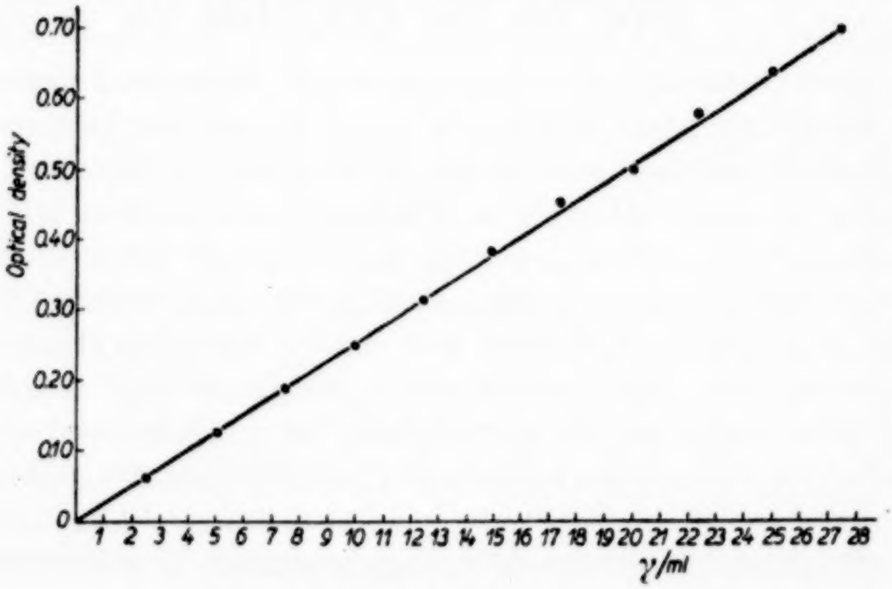

Fig. 6. Calibration curve.

SUMMARY

Meconic acid, a suitable reagent for the colorimetric determination of ferric iron, is presented. The nature of the chemical behaviour of the complex has been studied. The reagent must be used in acid medium (pH = 1). When the observation is made in Nessler's cylinder the sensitivity is one part in 5,000,000; in spot-plate the limit of identification is 0.5 microgram at a limiting concentration of 1:400,000. The colored complex obeys Beer's law over a useful range of iron concentration.

RÉSUMÉ

L'acide méconique est proposé comme réactif de l'ion ferrique. Les auteurs ont étudié la nature de l'ion complexe rouge; ce complexe se forme en solution acide (pH = 1). Lorsque la réaction se fait dans des cylindres de Nessler, la sensibilité est 1:5,000,000; sur la plaque de porcelaine à godets, la limite de perceptibilité est de 0.5 μg avec une concentration de 1:400,000. Le complexe coloré obéit à la loi de Beer dans un intervalle de concentration appréciable.

ZUSAMMENFASSUNG

Mekonsäure als wird Reagens für die kolorimetrische Bestimmung des Eisens (III) vorgeschlagen. Es wird das chemische Verhalten des Komplexes studiert. Das Reagens kann nur in saurem Medium (pH = 1) benützt werden. Wenn die Bestimmung im Nessler-Zylinder ausgeführt wird, erreicht man eine Empfindlichkeit von 1:5,000,000; auf der Tüpfelplatte ist die Erfassungsgrenze 0.5 μg bei einer Konzentration von 1:400,000. Der gefärbte Komplex folgt dem Beerschen Gesetz in einem nützlichen Bereich der Eisenkonzentration.

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COLORIMETRIC DETERMINATION OF TANTALUM IN TITANIUM ALLOYS

by

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INTRODUCTION

A considerable amount of metallurgical investigation has been conducted on tantalum-titanium alloys because of their desirable properties[1,8,18,20,29,30]. The study of this type of alloy, however, has been handicapped by the lack of suitable methods for the determination of the tantalum. The analysis of tantalum in the presence of titanium is an extremely difficult matter, especially when niobium is also present. Preliminary experimental work established that before tantalum could be determined in titanium alloys it must first be completely separated from the titanium. It was found that this could be accomplished by the use of two tannin precipitations with an intervening digestion with tannin. The use of a single tannin precipitation followed by a digestion with tannin, as used by NORWITZ, CODELL AND VERDERAME[23] in their procedure for the colorimetric determination of niobium in titanium alloys, was not satisfactory. The amount of titanium carried down by such a treatment, although having no effect on the colorimetric determination of niobium by thiocyanate, interfered with all methods for the direct determination of the tantalum.

Having established conditions for the separation of tantalum from the titanium, the next step was to consider the separation of the tantalum from niobium, or the determination of tantalum in the presence of niobium, since both of these elements are precipitated by tannin in a mineral acid medium. Tantalum-titanium alloys frequently contain small amounts of niobium. Many investigators have proposed procedures for the separation of tantalum from niobium MARIGNAC[6,19,21,27], based a separation of tantalum from niobium upon the fact that potassium tantalum fluoride is much less soluble in a dilute hydrofluoric acid solution than potassium niobium fluoride. POWELL AND SCHOELLER[26], and SCHOELLER[28] separated tantalum from niobium by precipitating the tantalum with tannin from a slightly acidified oxalate solution. The method required at least three precipitations. BHATTACHARYYA[5], CHARLOT[7], CUNNINGHAM[9] and WIRTZ[35] improved upon this tannin separation of tantalum from niobium by regulating the pH of the solution with bromophenol blue indicator. In the method of these investigators only one precipitation with tannin was made at this controlled pH. The precipitate was then ignited and the small amount of niobium remaining with the tantalum was determined by reduction in a Jones reductor and titration. WIRTZ[36] subsequently suggested the regulation of the pH with a potentiometer. HAYASHI[13] used alkaloids (cinchonine, brucine) together with tannin for the separation of tantalum from niobium. KLINGER, STENGEL AND WIRTZ[14] separated tantalum from niobium by use of a hydrochloric acid solution containing hydrogen peroxide. It was stated that under these conditions the niobium remained in solution while the tantalum was precipitated. FUCKE AND DAUBLÄNDER[10] separated tantalum from niobium by the use of phenylarsonic acid and hydrogen peroxide. The same investigators also used a solution containing sodium bicarbonate and hydrogen peroxide. WEISS AND LANDECKER[34] separated tantalum from niobium by passing carbon dioxide into a solution containing the two elements. The tantalum precipitated while the niobium remained in solution. ALIMARIN AND BUROVA[3] described a procedure for separating tantalum from niobium by the use of sodium hypophosphite in an oxalic acid-hydrochloric acid medium. MERRILL[22] separated tantalum from niobium by digesting the mixed oxides of the two elements with selenium oxychloride. The niobium dissolved while the tantalum remained behind. USPENSKAYA AND CHERNIKHOV[32] used potassium iodate to separate tantalum from niobium, while GILLIS, EECKHOUT AND POMA[11] used ferroin.

The above gravimetric methods were found to give results that left much to be desired. It seemed to the authors that the only satisfactory means for determining the tantalum was to use a colorimetric procedure. The only feasible colorimetric procedure that has been proposed is the pyrogallol method by which a yellow color is obtained in an acidic solution. The following media have been used for the colorimetric determination of tantalum by pyrogallol: bisulfate-ammonium oxalate[15,16,31], bisulfate-ammonium oxalate-sulfuric acid[2,4,24,25,33], bisulfate-ammonium oxalate-sulfuric acid-sulfite[17,24] and sulfuric acid-sulfite[12].

All the above media were tried in this laboratory and the bisulfate-ammonium oxalate medium was found to be the best. It was decided, therefore, to make a detailed study of this procedure. For this study aliquots of standard tantalum fluoride solution containing 2 mg of tantalum were treated with a few drops of sulfuric acid and the solutions evaporated to dryness in platinum crucibles. The residues were fused with potassium bisulfate and the melts taken up with ammonium oxalate solution. Solid pyrogallol was then added, the solutions diluted to 100 ml and the transmittance measured with a spectrophotometer. The effect of the amount of pyrogallol is shown in Fig. 1. The color increased rapidly in intensity until about 10 grams of pyrogallol had been added. At this point the color intensity started to level off. The use of 12 grams of pyrogallol (the same amount as has been suggested by THANHEISER[31]) is recommended. This is almost a saturated solution. The effect of the amount of bisulfate used is shown in Fig. 2. The use of 5 to 15 grams of potassium bisulfate gave about the same results for

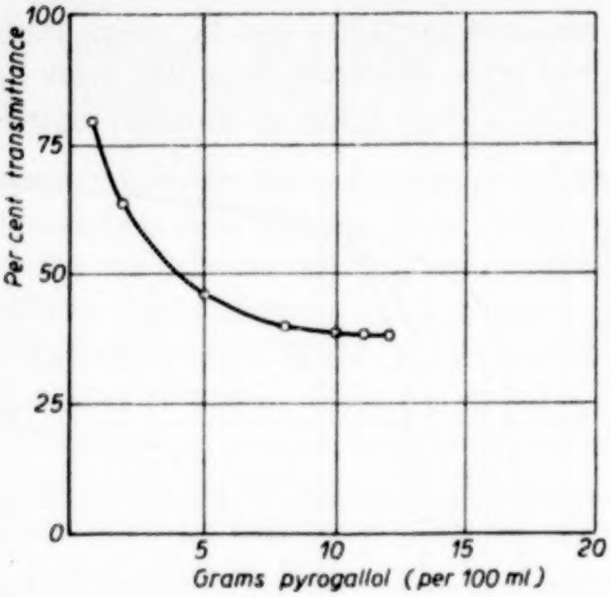

Fig. 1. Effect of amount of pyrogallol on tantalum pyrogallol color (water used as blank).

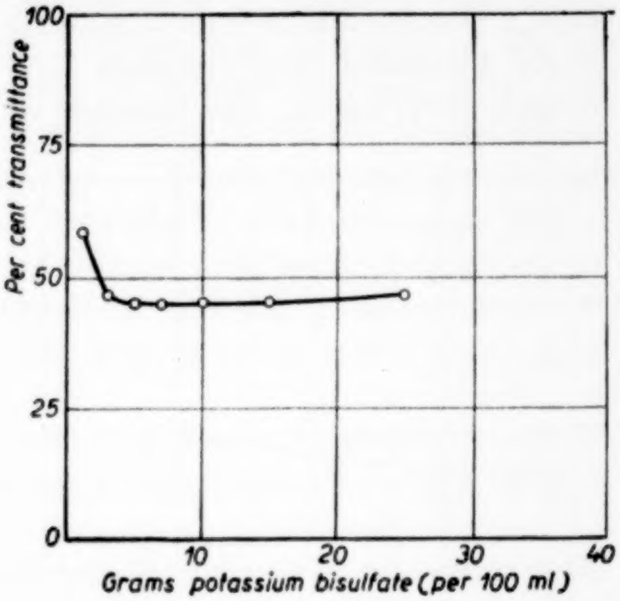

Fig. 2. Effect of amount of bisulfate on tantalum pyrogallol color.

tantalum. The use of less than 5 grams or more than 15 grams of potassium bisulfate gave low results for tantalum. The use of 7 grams of potassium bisulfate is recommended. The effect of the fusion time, using a Meeker burner, is shown in Fig. 3. The same result was obtained whether the heating was stopped as soon as the melt was clear or whether the heating was continued for three additional minutes. Heating for more than three minutes caused low results. The effect of the amount of ammonium oxalate was not investigated, since the maximum amount of ammonium oxalate should be present to ensure that the tantalum remains in solution. The spectrophotometric curves obtained for the tantalum pyrogallol color are shown in Fig. 4. It would seem that the color should be read at 400 millimicrons, the point of maximum absorption. However, better results were obtained at 420 millimicrons. It is to be noted that the blank pyrogallol solution gives significant absorption. The blank shown in Fig. 3 was obtained using the purest pyrogallol obtainable. This blank solution was almost colorless. Pyrogallol obtained from some sources was found to give too dark a blank (yellow or light pink). The best pyrogallol is that which consists of white shiny crystals. It is best to avoid material that is grey or powdery.

The tantalum pyrogallol color was found to be stable for several hours. In experimenting with pure solutions it was found that 0.05 gram of niobium did not give an interfering color, nor did it affect the tantalum color in any way. However, in working with the actual procedure for titanium alloys it was found that more than 0.0025 gram of niobium interfered with the method by causing occlusion of the titanium by the tannin precipitate. This caused high results for tantalum since titanium gives a yellow color with pyrogallol. The fact that in tannin precipitations from a mineral acid medium tantalum can be much more easily separated from titanium than niobium from titanium does not seem to be generally known. The presence of more than 0.0050 gram of tungsten causes high results for the tantalum, because the tungsten is partially precipitated by the tannin and reacts with the pyrogallol to give a yellow color. The proposed method is recommended for tantalum-titanium alloys containing 0.05 to 5 per cent. tantalum.

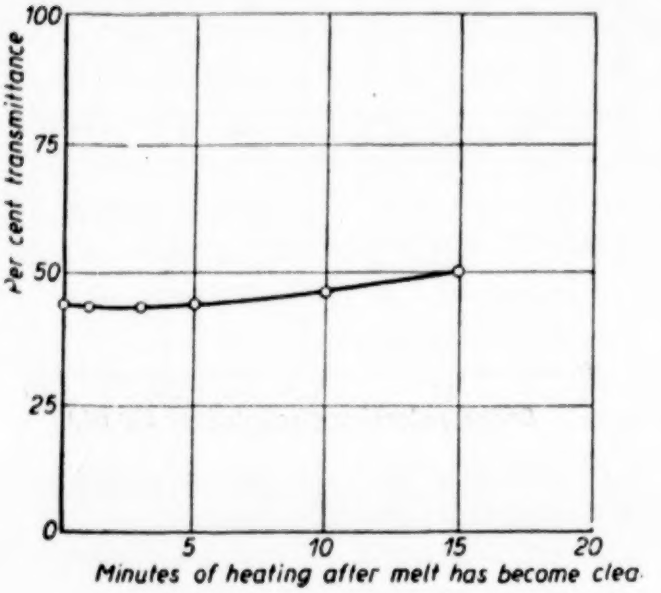

Fig. 3. Effect of fusion time on tantalum pyrogallol color.

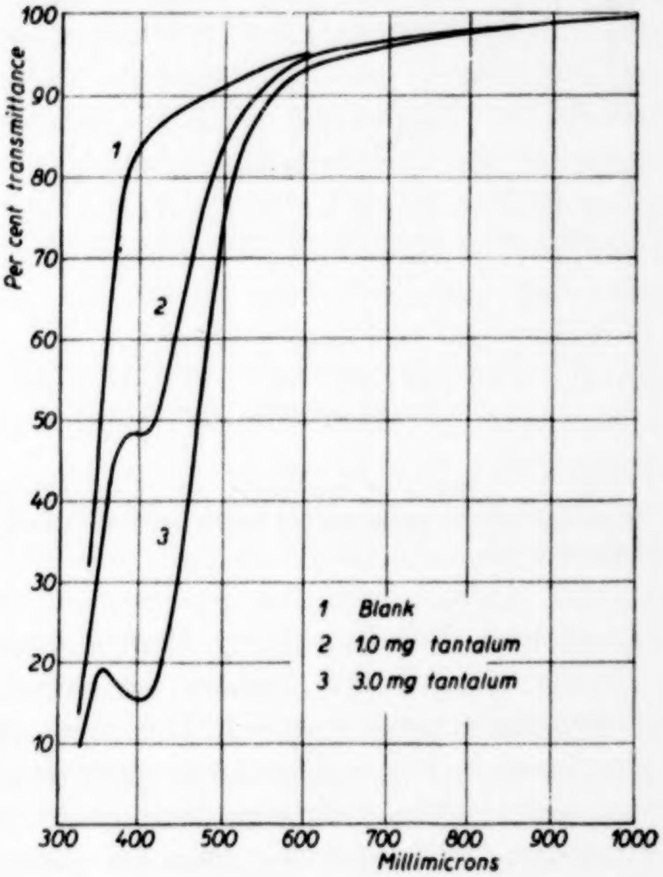

Fig. 4. Spectrophotometric curves for tantalum pyrogallol color.

APPARATUS AND REAGENTS

Beckman Model B Spectrophotometer with four one-cm matched cells

Tannin (tannic acid), cp

Pyrogallol, cp

Boric acid, cp

Potassium bisulfate, fused lumps, cp

Ammonium oxalate, cp

Hydrochloric acid, sp gr 1.18

Hydrofluoric acid, 50 per cent.

Nitric acid, sp gr 1.42

Sulfuric acid, sp gr 1.84

Standard tantalum solution (1 ml = 1.00 mg tantalum). Transfer 1.0000 gram tantalum metal to a covered 30 ml platinum crucible, and add 5 ml of water. Add hydrofluoric acid and nitric acid dropwise to dissolve the tantalum. Use about 5 drops of hydrofluoric acid to 1 drop of nitric acid. When the tantalum has dissolved wash down the cover lid and remove it. Warm the crucible on the hot plate a few minutes. Cool. Add 15 ml of hydrofluoric acid and wash into a beaker containing 400 ml of water, 15 ml of hydrofluoric acid, and 20 ml of sulfuric acid. Transfer to a 1-liter volumetric flask and dilute to the mark.

Tannin wash solution. Add 5 grams of tannin and 25 ml of hydrochloric acid to 1 liter of water. Make fresh daily.

Ammonium oxalate solution (4 per cent.). Add 80 grams of ammonium oxalate to about 1 liter of water and dilute to 2 liters with water. Allow to stand several hours with occasional shaking to dissolve.

Blank solution. Fuse 200 grams of potassium bisulfate in a large platinum dish. Allow to cool. Dissolve the melt in about 1500 ml of water by heating on the hot plate. Allow to cool somewhat. Add 80 grams of ammonium oxalate and stir to dissolve. Cool and dilute to 2 liters with water.

METHOD

Preparation of calibration curve

Transfer 0.25, 1, 2, 3, 4 and 5 ml aliquots of Standard Tantalum Solution measured with an accurate 10 ml microburette to 30 ml platinum crucibles. Add 5 drops of sulfuric acid and evaporate to dryness on the hot plate. Continue

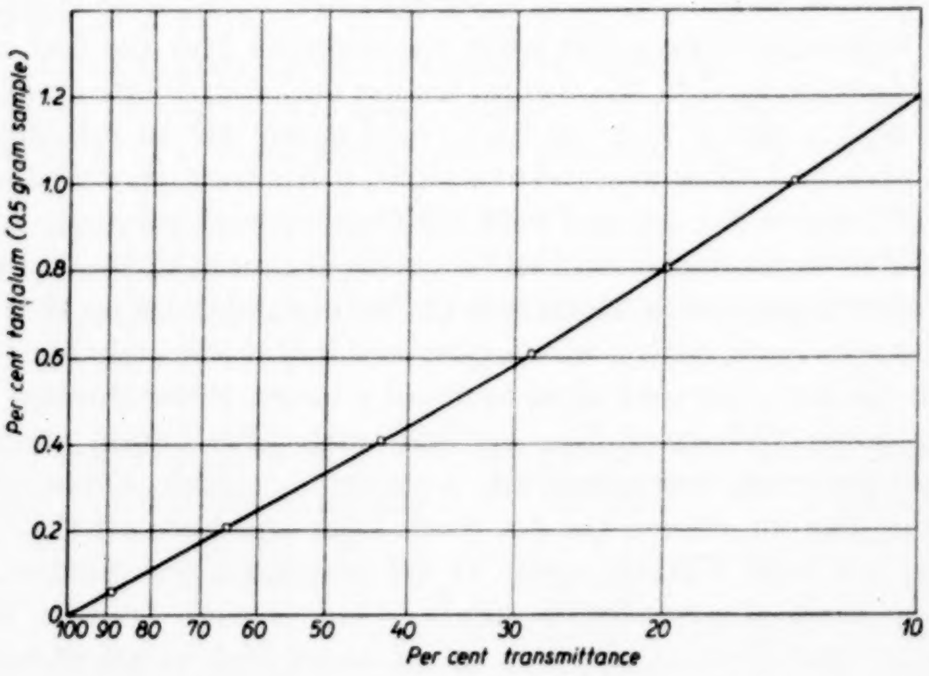

Fig. 5. Calibration curve for tantalum pyrogallol color.

heating until no more fumes of sulfuric acid appear. Fuse with 7 grams potassium bisulfate. Allow to cool. Transfer the melts to 250 ml beakers containing 70 ml of ammonium oxalate solution (4 per cent.). Warm on the hot plate at about 70° to 80° C with occasional stirring until the melts have dissolved. Wash down and remove the platinum crucibles. Cool to room temperature. Add 12 grams of pyrogallol and allow to stand for a few minutes with occasional stirring to dissolve. Transfer to 100 ml volumetric flasks and dilute to the mark with water. Measure the transmittance at 420 millimicrons with a spectrophotometer. Set the spectrophotometer at 100 per cent. transmittance with a reagent blank prepared by adding 12 grams of pyrogallol to 70 ml of blank solution and diluting to 100 ml with water. Plot the per cent. transmittance against per cent. tantalum. For a 0.5 gram sample 1 ml of standard tantalum solution is equivalent to 0.2 per cent. tantalum. The calibration curve obtained by the authors is shown in Fig. 5.

Procedure

Transfer 0.5 gram of the sample to a covered 30 ml platinum crucible and add 5 ml of water. Add hydrofluoric acid and nitric acid dropwise to dissolve the sample. Use about 5 drops of hydrofluoric acid to 1 drop of nitric acid. Enough nitric acid should be present at the end of the reaction to ensure that the titanium is oxidized to the titanic state. After the reaction is complete, wash down the cover lid and remove it. Heat over an asbestos pad on the hot plate until the volume is reduced to about 3 ml. Remove from the hot plate and allow to cool to room temperature. Add 3 ml of water and 3 ml of hydrochloric acid. Wash the contents of the crucible into a 600 ml beaker containing 100 ml of water and 2 grams of tannin. Add 2 ml of water and 2 ml of hydrochloric acid to the crucible. Swab the crucible with a policeman and wash the contents into the 600 ml beaker. Add 8 grams of boric acid to the 600 ml beaker and stir. Dilute to 250 ml with water, cover with a watch glass and boil moderately for 10 minutes. Remove from the hot plate and allow to stand overnight. Filter through a medium texture filter paper (Whatman No. 40) and wash with tannin wash solution. Add 240 ml of water, 10 ml of hydrochloric acid and 2 grams of tannin to the 600 ml beaker. Transfer the filter paper and precipitate to the beaker and break up the filter paper with a stirring rod. Cover with a watch glass and boil moderately for 15 minutes. Remove from the hot plate and allow to stand 2 hours. Filter through a medium texture filter paper (Whatman No. 40) and wash with tannin wash solution. Place the filter paper and precipitate into a platinum crucible. Drive off the moisture by heating the crucible on the hot plate. Char and burn off the filter paper by igniting at low heat. Finally, ignite at red heat for a few minutes.

Fuse with 5 grams of potassium bisulfate. Allow to cool. Transfer the melt to a clean 600 ml beaker containing 100 ml of water and 10 ml of hydrochloric acid. Do not use the original 600 ml beaker unless it has been cleaned with dichromate-sulfuric acid cleaning solution. Warm on the hot plate at about 70° to 80° C with occasional stirring until the melt has dissolved. Wash and remove the platinum crucible. Dilute to 250 ml with water and add 0.5 gram of tannin. Heat to boiling and boil moderately for 10 minutes. Remove from the hot plate and allow to stand 2 hours. Filter through a medium texture filter paper (Whatman No. 40) containing a little paper pulp, and wash with tannin wash solution. Place the filter paper and precipitate into a platinum crucible. Drive off the moisture by heating the crucible on the hot plate. Char and burn off the filter paper by igniting at low heat. Finally ignite at red heat for a few minutes.

Fuse with 7 grams of potassium bisulfate. Allow to cool. Transfer the melt to a 250 ml beaker containing 70 ml of ammonium oxalate solution (4 per cent.). Warm on the hot plate at about 70° to 90° C with occasional stirring until the melt has dissolved. Wash down and remove the platinum crucible. Allow to cool to room temperature. If the sample contains less than 1 per cent. tantalum, use the whole sample at this stage. If the sample contains more than 1 per cent. tantalum, transfer the solution to a 100 ml volumetric flask and dilute to the mark with water. Pipette an aliquot of the solution into the original 250 ml beaker. For a tantalum content of 1 to 3 per cent. use a 25 aliquot; for a tantalum content of 3 to 5 per cent. tantalum use a 10 ml aliquot. If a 25 ml aliquot is used, add 53 ml of blank solution to the 250 ml beaker. If a 10 ml aliquot is used, add 63 ml of blank solution.

Add 12 grams of pyrogallol and allow to stand for a few minutes with occasional stirring to dissolve. Transfer to a 100 ml volumetric flask and dilute to the mark. Measure the transmittance at 420 millimicrons in a spectrophotometer. Set the spectrophotometer at 100 per cent. transmittance with a reagent blank prepared by adding 12 grams of pyrogallol to 70 ml of blank solution and dilute to 100 ml with water. Convert the readings to per cent. tantalum by consulting the calibration curve. If a 25 ml aliquot was used, multiply the result as read from the calibration curve by 4. If a 10 ml aliquot was used, multiply the result by 10.

RESULTS

The results obtained for tantalum in synthetic tantalum-titanium alloys prepared by adding Standard Tantalum Solution to titanium metal are shown in Table I. The results obtained in the presence of possible interfering elements are shown

TABLE I
RESULTS FOR TANTALUM IN SYNTHETIC TANTALUM-TITANIUM ALLOYS

Tantalum added (%)	Average tantalum found (%)	Std dev (%)	Number of determinations
0.050	0.046	0.005	5
0.400	0.402	0.012	6
1.00	1.01	0.020	5
2.00	1.99	0.047	5
5.00	5.06	0.11	5

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in Table II. The results obtained for a special tantalum-niobium-titanium alloy containing approximately 1 per cent tantalum and 1 per cent niobium are shown in Table III. For this special alloy a 0.25 gram sample was used in order to reduce the niobium content to the permissible limit.

TABLE II

RESULTS FOR TANTALUM IN THE PRESENCE OF POSSIBLE INTERFERENCES

Element added	Amount added (%)	Added as	Tantalum added (%)	Tantalum found (%)
Niobium	0.5	Standard niobium solution	0.00	0.00
,,	,,	,,	0.40	0.42
,,	,,	,,	1.00	1.02
Tungsten	1.0	$Na_2WO_4.2H_2O$	0.00	0.00
,,	,,	,,	0.40	0.39
,,	,,	,,	1.00	1.03
Iron	10	Metallic Fe	0.40	0.40
Chromium	10	$Cr_2(SO_4)_3$	0.40	0.41
Molybdenum	10	$(NH_4)_6Mo_7O_{24}.4H_2O$	0.40	0.39
Manganese	10	$MnSO_4.H_2O$	0.40	0.40
Vanadium	5	$(VO)_2Cl_4$	0.40	0.38
Silicon	5	$Na_2SiO_3.9H_2O$	0.40	0.41
Aluminum	5	$Al_2(SO_4)_3.18H_2O$	0.40	0.40
Copper	5	$CuSO_4.5H_2O$	0.40	0.39
Cobalt	5	$CoCl_2.6H_2O$	0.40	0.42
Nickel	5	$NiCl_2.6H_2O$	0.40	0.41
Tin	5	$SnCl_2.2H_2O$	0.40	0.40
Magnesium	5	$MgSO_4.7H_2O$	0.40	0.39
Calcium	5	$CaCl_2.2H_2O$	0.40	0.40
Boron	1	H_3BO_3	0.40	0.41
Phosphorus	1	$(NH_4)_2HPO_4$	0.40	0.40

TABLE III

RESULTS FOR TANTALUM IN A SPECIAL TANTALUM-NIOBIUM-TITANIUM ALLOY CONTAINING APPROXIMATELY 1 PER CENT. TANTALUM AND 1 PER CENT. NIOBIUM

	(0.25 gram sample) Tantalum found (%)
	0.92
	0.90
	0.94
	0.92
	0.92
Average (%)	0.92
Standard deviation (%)	0.014

ACKNOWLEDGEMENT

The authors are indebted to FRANK D. VERDERAME for his assistance with some of the preliminary experimental work.

References p. 182.

SUMMARY

Experimental work on tantalum-titanium alloys has been handicapped by the lack of accurate methods for the determination of the tantalum. In this paper a colorimetric procedure is proposed for the determination. The tantalum is separated completely from the titanium by two tannin precipitations with an intervening digestion with tannin. The tannin precipitate is ignited, fused with potassium bisulfate and the melt taken up with ammonium oxalate solution. Pyrogallol is then added and the intensity of the yellow color is measured. A study was made of the tantalum pyrogallol color to obtain optimum conditions. Elements that would be found in the usual tantalum-titanium alloys do not interfere with the method. More than 0.0025 gram of niobium interferes by causing occlusion of titanium by the tannin precipitate. This causes high results for tantalum, since titanium reacts with pyrogallol to produce a yellow color. The presence of more than 0.0050 gram of tungsten causes high results for tantalum because tungsten is partially precipitated by the tannin and reacts with pyrogallol to produce a yellow color. The proposed method is recommended for tantalum-titanium alloys containing 0.05 to 5 per cent. tantalum.

RÉSUMÉ

Une étude expérimentale sur les alliages tantale-titane est rendue difficile par le manque de méthodes précises pour le dosage du tantale. Les auteurs proposent la méthode colorimétrique suivante. Le tantale est séparé quantitativement du titane par une double précipitation au tannin. Le précipité ainsi obtenu est calciné et fondu avec le bisulfate de potassium. Puis le produit fondu est traité par une solution d'oxalate d'ammonium. On ajoute ensuite du pyrogallol et on mesure l'intensité de la coloration jaune obtenue. Une étude a été faite sur la coloration tantale-pyrogallol pour obtenir les conditions optima. Les éléments habituellement présents dans les alliages tantale-titane ne gênent pas. Des quantités de niobium supérieures à 0.0025 g gênent: il peut se former des occlusions de titane dans le précipité de tannin, conduisant à des résultats trop élevés pour le tantale; en effet le titane réagit également avec le pyrogallol en donnant une coloration jaune. Il en est de même pour le tungstène, en quantités supérieures à 0.005 g, cet élément précipitant partiellement avec le tannin et donnant une coloration jaune avec le pyrogallol. La méthode proposée est recommandée pour des alliages tantale-titane renfermant 0.05 à 5% de tantale.

ZUSAMMENFASSUNG

Experimentelle Arbeiten mit Tantal-Titan-Legierungen wurden durch den Mangel an genauen Tantalbestimmungsmethoden gehemmt. In dieser Arbeit wird ein kolorimetrisches Verfahren zur Bestimmung vorgeschlagen. Tantal wird durch zwei Tanninausfällungen und dazwischen durch eine Digerierung mit Tannin vollständig vom Titan abgetrennt. Der Tanninniederschlag wird geglüht, mit Kaliumbisulfat geschmolzen und die Schmelze mit Ammoniumoxalatlösung aufgenommen. Dann wird Pyrogallol hinzugefügt und die Intensität der gelben Färbung gemessen. Es wurde eine Untersuchung der Tantal-Pyrogallol-Färbung durchgeführt um optimale Bedingungen zu erhalten. In gewöhnlichen Tantal-Titan-Legierungen vorhandene Elemente stören bei dieser Methode nicht. Mehr als 0.0025 g Niob stört, da es eine Einschliessung von Titan im Tanninniederschlag verursacht. Dies führt zu zu hohen Werten für Tantal, da Titan mit Pyrogallol reagiert und eine gelbe Färbung entsteht. Die Gegenwart von mehr als 0.0050 g Wolfram verursacht zu hohe Tantalwerte, da Wolfram teilweise von Tannin gefällt wird und mit Pyrogallol reagiert und eine gelbe Färbung ergibt. Die vorgeschlagene Methode wird für Tantal-Titan-Legierungen empfohlen, die 0.05 — 5% Tantal enthalten.

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PHOTOMETRIC DETERMINATION OF PHOSPHORUS IN SILICATE ROCKS

by

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The method commonly used for determining phosphorus in rocks involves precipitation as ammonium phosphomolybdate and weighing as such or as magnesium pyrophosphate after ignition. Although this method gives accurate results when properly carried out, a shorter and simpler method of equal or superior accuracy would be useful. Results reported here (Tables I and II) show that the colorimetric procedure first proposed by MISSON[1] for phosphorus in steel can be applied satisfactorily to rocks. This procedure depends upon the formation of a soluble yellow molybdovanadophosphoric acid complex. MISSON's method has already been used by SHAPIRO AND BRANNOCK[2] for the rapid, rough determination of phosphorus in rocks; they report percentages of P_2O_5 to the first decimal only.

In brief, the present procedure involves decomposition of the sample with nitric-hydrofluoric acid, formation of the colored complex in nitric acid solution, and measurement with a spectrophotometer or filter photometer. The conditions of the determination are similar to earlier modifications of Misson's procedure[3].

Special solutions

Ammonium molybdate, 5 per cent. Dissolve 50 g of reagent-grade $(NH_4)_6Mo_7O_{24}.4H_2O$ in 500 ml of warm water. Allow the solution to stand overnight, filter if not entirely clear, and dilute to 1 liter.

Ammonium metavanadate, 0.25 per cent. Dissolve 2.5 g of NH_4VO_3 in 500 ml of hot water, cool, and add 20 ml of concentrated nitric acid. Allow to stand overnight, filter if not clear, and dilute to 1 liter.

Standard phosphate solution, 1.00 mg P_2O_5 per ml. Dissolve 0.899 g of KH_2PO_4 (recrystallized and dried at 100°) in water and dilute to 500 ml. This solution may be further diluted as convenient.

Procedure

Weigh 0.5 g of 100-mesh rock powder (0.01 to 1 per cent. P_2O_5) into a platinum dish and moisten with a milliliter of water. Add 4 ml of concentrated nitric acid,

TABLE I

PHOTOMETRIC DETERMINATION OF PHOSPHORUS IN SILICATE ROCKS

Sample	P_2O_5 present %	P_2O_5 found %
Granite[a]	0.022	0.026, 0.026
Granite	0.032	0.038, 0.033
Granite	0.112	0.119, 0.116
Granite	0.212	0.210, 0,218
Granite	0.412	0.418, 0.416, 0.408, 0.412
Granite	0.612	0.608, 0.606, 0.602, 0.606
Granite	0.812	0.806, 0.806, 0.803, 0.803
Granite	1.012	0.991, 0.998, 1.007, 1.000
Granite, 1.0% TiO_2	0.022	0.026
Granite, 1.0% TiO_2	0.512	0.510
Granite, 1.0% TiO_2	1.012	0.994
Granite, 0.11% ZrO_2	0.062	0.062
Granite, 0.11% ZrO_2	0.212	0.216
Synthetic subsilicic rock[b]	0.074	0.074, 0.074
Synthetic subsilicic rock	0.134	0.134, 0.134
Synthetic subsilicic rock	0.234	0.234, 0.236
Synthetic subsilicic rock	0.334	0.335, 0.333
Synthetic subsilicic rock	0.534	0.538
Synthetic subsilicic rock	0.834	0.838, 0.833
Synthetic subsilicic rock	1.034	1.032, 1.036
NBS Standard Sample No. 70 (potash feldspar)	0.012	0.014
NBS Standard Sample No. 99 (soda feldspar)	0.142	0.164
NBS Standard Sample No. 97 (flint clay)	0.08	0.082, 0.086

[a] Contained 0.012% P_2O_5 originally as determined photometrically (average of 0.015, 0.012, 0.012, 0.010 and 0.011%). Phosphorus added as KH_2PO_4. Bulk composition of sample that of a typical granite.

[b] Partial percentage composition: SiO_2 48.0, Al_2O_3 13.0, Fe_2O_3 12.0, FeO 0.8, MgO 6.8, CaO 10.1, TiO_2 1.66, MnO 0.12. Original P_2O_5 content 0.034% (average of 0.035, 0.035 and 0.033).

TABLE II

COMPARISON OF DETERMINATION OF PHOSPHORUS BY GRAVIMETRIC AND PHOTOMETRIC METHODS

Sample	P_2O_5, %	
	Gravimetric[a]	Photometric
Pegmatite	0.08	0.092
Andesite	0.14	0.148
Diabase	0.15	0.17
Granodiorite	0.39	0.39
Diorite	0.41	0.42
Pegmatite	0.47	0.48
Peridotite	0.74	0.77

[a] Weighing as ammonium phosphomolybdate. Values from files of University of Minnesota Rock Analysis Laboratory.

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using a cover glass to prevent loss if carbon dioxide is evolved. Then add 5 ml of hydrofluoric acid and mix by careful swirling or by stirring with a platinum wire. Slowly evaporate to dryness on a hot plate or in a radiator, preferably with occasional stirring at the beginning to prevent caking of the powder. Bake the residue briefly at a temperature below 250° C. Cool, add 4 ml of nitric acid, break up the residue, and add 2 ml of hydrofluoric acid. Evaporate and bake as before. Finally add 4 ml of nitric acid, disintegrate the residue, evaporate, and bake for 30 minutes to expel hydrofluoric acid.

Moisten the residue with water and take up in 4 ml of concentrated nitric acid (free from oxides of nitrogen) and transfer to a small beaker. Dilute to about 25 ml and digest on the steam bath until solid material has been brought into solution. Rocks high in titanium may give a turbid solution, which then should be boiled for a few minutes to produce a filterable precipitate. Filter through a retentive paper, wash with a little water containing a few drops of nitric acid, and dilute filtrate and washings to 50 ml in a volumetric flask.

By means of a dry pipet, transfer 25 ml of the solution to a 50 ml volumetric flask and add 5.0 ml each of ammonium vanadate and ammonium molybdate solution, in that order. Mix, allow to stand at room temperature for 30 minutes, and measure the transmittancy of the solution in a 1 cm cell at 460 mμ in a spectrophotometer or in a filter photometer with a filter having maximum transmission near this wavelength.

Obtain the correction for absorption by ferric iron or any other colored substance in the solution by diluting the remaining 25 ml of sample solution (the loss of a few drops from pipetting the first aliquot is usually of no importance) to 50 ml and finding log I_0/I. Also obtain the correction for the reagent blank by evaporating to dryness the same volumes of hydrofluoric and nitric acids used for the sample, adding ammonium vanadate and molybdate, and measuring the transmittancy. Usually the greater part of the blank correction is due to absorption by the reagent mixture. If the phosphorus content of the acids used in the decomposition is negligibly small, the blank correction is obtained automatically if the transmittancy of the sample solution treated with reagent is measured against the diluted reagent in the reference cell. Find the P_2O_5 content of the sample solution by reference to a standard curve.

Comments on procedure

Results are low if the residue from the decomposition of the sample is baked at too high a temperature. A temperature of 200 to 250° C is safe. Low results are thought to be due to volatilization of phosphorus rather than pyrophosphate formation.

The most favorable wavelength for measurement of absorption by the phosphorus complex is about 460 mμ. At wavelengths below 450 mμ the absorbance of the reagent is undesirably great, and at wave lenghts above 470 mμ sensitivity is impaired. With a Beckman Model B spectrophotometer the following values of log I_0/I (1 cm) were found:

	Reagent blank	P complex (10 p.p.m. $P_2O_5 = 0.2\%$ in 0.5 g sample)
450 mμ	0.009	0.106
460 mμ	0.006	0.089
470 mμ	0.004	0.074

The absorbance due to ferric iron is very small at 460 mμ, amounting to about 0.003 for a 0.5 g sample containing 30 per cent. Fe_2O_3. This absorbance is equivalent to approximately 0.007 per cent. P_2O_5. Since the iron content is usually not more than 15 per cent. Fe_2O_3, the error due to iron is not likely to exceed 0.005 per cent. P_2O_5. However, the error due to ferric iron and any other inert colored substance is easily avoided by obtaining the absorbance of an aliquot of the sample solution not treated with reagent.

Although the phosphorus complex follows Beer's law up to at least 50 p.p.m. P_2O_5, apparent deviation may be found with a filter photometer. With a Leitz-Rouy filter photometer (460 mμ filter), a linear relation between the concentration of phosphorus and log I_0/I was found up to about 10 p.p.m. P_2O_5 in solution.

The effect of arsenic rarely needs to be considered, because its amount in rocks seldom rises to 0.01 per cent. and it gives less color with the reagent than does phosphorus; moreover, some arsenic is volatilized in the decomposition. Silicon, which might be introduced from the glassware, forms a much less strongly colored heteropoly acid than phosphorus under the conditions, and this source of error can be disregarded except in the most exact work. Germanium occurs in rocks in such minute amounts that it is not an interfering element, although it does form a molybdovanadic complex, which, however, is less strongly colored than the phosphorus complex.

Titanium in amounts as high as 1.6 per cent. TiO_2 and zirconium as high as 0.1 per cent. ZrO_2 do not cause error.

It appears from the present results that 0.01 to 1.0 per cent. of P_2O_5 can be determined to within 0.01 per cent., or better in the lower part of the range. If necessary the size of sample can readily be reduced to 0.1 g by using a final volume of 10 ml instead of 50 ml.

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SUMMARY

Phosphorus in silicate rocks may bedeterminedaccurately by the photometric molybdovanadophosphoric acid method following decomposition of the sample with nitric-hydrofluoric acid.

RÉSUMÉ

Le phosphore des roches silicatées peut être dosé photométriquement avec précision sous forme d'acide molybdovanadophosphorique; l'échantillon est préalablement attaqué par un mélange d'acides nitrique et fluorhydrique.

ZUSAMMENFASSUNG

Der Phosphor kann in Silikatgesteinen mit Hilfe der photometrischen Methode als Molybdovanadophosphorsäure genau bestimmt werden; hierzu wird die Probe erst mit Salpetersäure und Fluorwasserstoffsäure aufgeschlossen.

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HETEROMETRIC MICRO-DETERMINATION OF URANIUM(VI) BY PRECIPITATION AS PHOSPHATE

by

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The aim of this work is to present a method for the micro-quantitative precipitation of uranium(VI) as phosphate, taking advantage of a gravimetric method without carrying out a separation and weighing. The heterometric method developed by the first author and co-workers, was used instead. Only a few milligrams of uranium (1-8 mg) in a volume of 10 ml are necessary, and the accuracy of determination is about ± 0.01 mg. With some experience even better results may be obtained. Generally, a titration takes about 15 min.

A series of experiments was made and a selection of the results is given in the form of curves (Figs. 1 and 2) and tables. (The table gives the numerical values of the experiments, while the curves show the course of titration of the corresponding experiments). Preliminary titrations showed that direct titration of U(VI) ($UO_2(NO_3)_2$) with phosphate alone does not give satisfactory results.

EXPERIMENTAL

All details concerning the Heterometer and heterometric titrations have been given elsewhere [1-7]. The chemicals used were all c.p. Baker analysed reagents.

RESULTS

Titrations of uranium nitrate solutions with Na_2HPO_4 in the presence of NH_4Cl gave no satisfactory results. Some titrations in the presence of NH_4Cl are given in Fig. 1, curves 2 and 3, and the calculations are compiled in Table I (exp. 1-3). The best results are obtained in the presence of both NH_4Cl and acetic acid. The presence of acetic acid raises the maximum optical density values (and hence sensitivity) and the accuracy. The addition of alcohol decreases the maximum density values and makes the results less certain. The titration proceeds quickly and readings on the galvanometer become constant in a few seconds. The whole titration lasts less than 15 minutes. As experiment 2 (Table I and Fig. 1, curve 2) shows, theoretical values for uranium may be obtained.

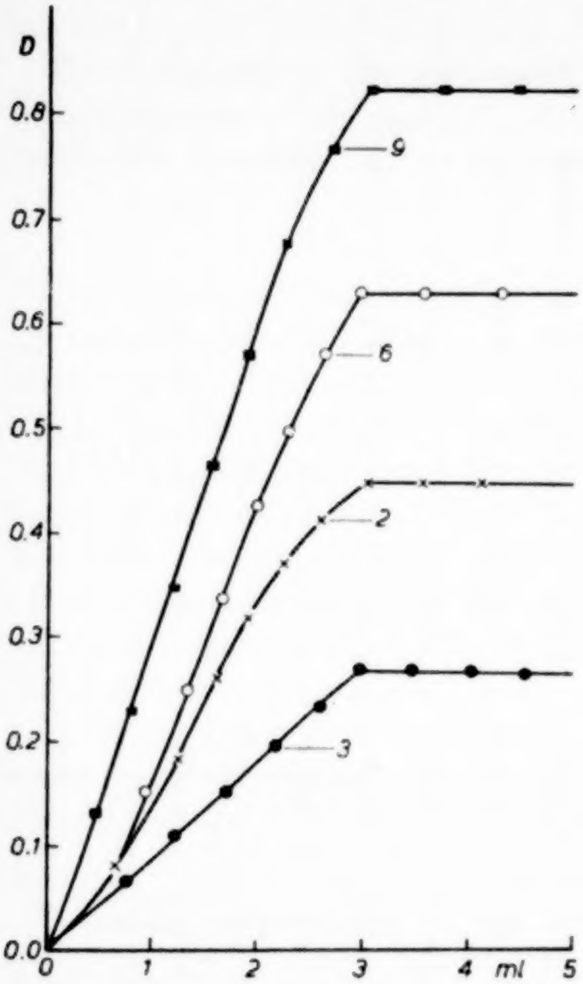

Fig. 1
(Explanation in text)

Additional experiments were made with the purpose of increasing the sensitivity of the heterometric titration towards smaller quantities of uranium. NH_4Cl was replaced by other basic nitrogen compounds.

Hexamethylenetetramine and ethylenediamine. Some results are given in Table I (exps. 4 and 5). No advantages could be obtained and an excess of the reagent (ethylenediamine) interferes with the results.

Pyridine. (See Table I, exps. 6 and 7, and curves 6 and 7). The maximum optical densities are somewhat higher than in the case of NH_4Cl, therefore somewhat smaller quantities of uranium may be analysed. The absolute error amounts to 0.01 mg for a solution of 0.001*M* uranium (exp. 7). The time required for a full titration generally increases with the decreasing concentration of uranium analysed. The titration lasted (exp. 7) about half an hour.

Quinoline or quinine. In the presence of quinine (exp. 8), even a solution of 0.0005*M* uranium could be analysed, but the time required was about 50 minutes. In the presence of quinoline (exps. 9-11) the maximum density is higher than with NH_4Cl. A 0.001*M* solution could be used and the errors were small or nil, but the time of titration was about 30-40 minutes.

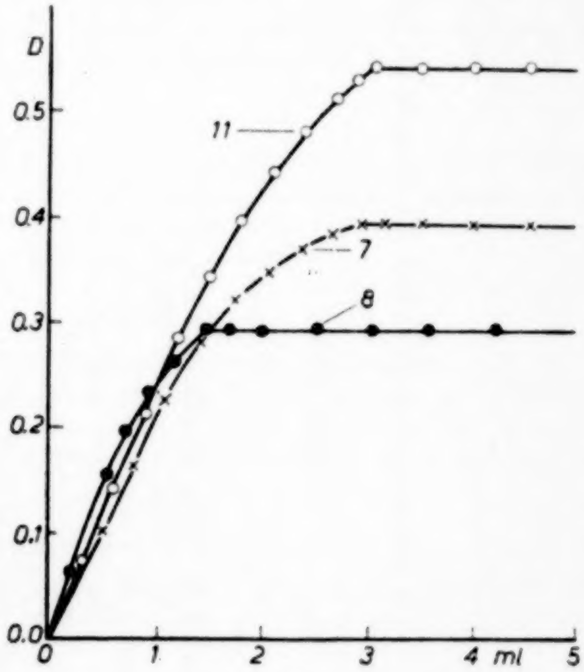

Fig. 2
(Explanation in text)

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TABLE I

GENERAL COMPOSITION: 3 ml n*M* $UO_2(NO_3)_2$ + 7 ml SOLUTION + X ml m*M* Na_2HPO_4.

Exper. number	Solution	$UO_2(NO_3)_2$ molar.	Uranium in mg	Na_2HPO_4 used		Density maxim.	error	
				ml	molar		mg	γ per ml
1	1 ml 1*M* CH_3COOH + 2 ml 1*M* NH_4Cl + 4 ml alcohol	0.01	7.1442	2.90	0.01	0.184	—0.25	25
2	1 ml 1*M* CH_3COOH + 2 ml 1*M* NH_4Cl + 4 ml H_2O	0.01	7.1442	3.00	0.01	0.450	0.0	0.0
3	2 ml 1*M* NH_4Cl + 5 ml H_2O	0.01	7.1442	2.95	0.01	0.268	—0.12	12
4	1 ml 1*M* CH_3COOH + 3 ml 0.1*M* ethylenediam. + 3 ml H_2O	0.01	7.1442	3.00	0.01	0.233	0.0	0.0
5	2 ml 1*M* CH_3COOH + 0.5 ml 1*M* hexamethylened. + 4.5 ml H_2O	0.01	7.1442	2.95	0.01	0.374	—0.12	12
6	2 ml 1*M* CH_3COOH + 5 ml 0.2*M* pyridine	0.01	7.1442	2.95	0.01	0.629	—0.12	12
7	2 ml 1*M* CH_3COOH + 5 ml 0.2*M* pyridine	0.004	2.8577	2.90	0.004	0.392	—0.1	10
8	2 ml 1*M* CH_3COOH + 5 ml 0.1*M* quinine. HCl	0.002	1.4288	1.45	0.004	0.292	—0.05	5
9	2 ml 1*M* CH_3COOH + 0.5 ml 1*M* quinoline + 4.5 ml H_2O	0.01	7.1442	3.05	0.01	0.824	+0.12	12
10	2 ml 1*M* CH_3COOH + 0.5 ml 1*M* quinoline + 4.5 ml alc.	0.004	2.8577	3.05	0.004	0.462	+0.05	5
11	2 ml 1*M* CH_3COOH + 0.5 ml 1*M* quinoline + 4.5 ml H_2O	0.004	2.8577	3.00	0.004	0.539	0.0	0.0

CONCLUSION

From the above, the following conclusions may be drawn: a water solution which contains a few mg (1-8) of uranium in a volume of 10 ml may be heterometrically titrated with an accuracy of 0.01 to 0.02 mg.

METHOD

To a solution which contains a few mg uranium(VI) in a volume of 10 ml, are added 0.5 ml 4*M* NH_4Cl or definite quantities of pyridine, quinoline or quinine. A few drops of concentrated acetic acid are added (final concentration of free acetic acid should be about 0.1*M*). A standardised solution of 0.01*M* — 0.004*M* Na_2HPO_4 is added drop by drop from a microburet, while the solution is stirred vigorously. The readings of the galvanometer are taken when they become constant. The first maximum optical density point which corresponds to the endpoint is taken either from a graph (enlarged), by drawing a line through the maxima values obtained, or derived from the numerical values near the maximum. Where the quantity of the analysed metal is unknown, it is advisable to make a preliminary rough heterometric titration, taking only a few points and only then to make the final titration. Special attention is given to the points near the maximum optical density.

SUMMARY

A method is presented for the heterometric determination of uranium(VI) by titration with a solution of Na_2HPO_4. 1-8 mg uranium in 10 ml solution can be determined with an accuracy of 0.01 mg in about 15 minutes. The influence of various nitrogen compounds and different working conditions were studied.

RÉSUMÉ

Une méthode est présentée pour la détermination hétérométrique de l'uranium (VI) par titration au moyen d'une solution de Na_2HPO_4. 1-8 mg d'uranium dans 10 ml de solution peuvent être déterminés en 15 minutes environ. L'influence des dérivés azotés et des conditions de travail ont été étudiées.

ZUSAMMENFASSUNG

Eine Methode zur heterometrischen Bestimmung von Uranium(VI) durch Titration mit einer Na_2HPO_4 Lösung wird gebracht. 1-8 mg Uranium können in 10 ml Lösung mit einer Genauigkeit von 0.01 mg in etwa 15 Minuten bestimmt werden. Der Einfluss von verschiedenen Stickstoffverbindungen und den anderen Arbeitsbedingungen wurden studiert.

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FORMIC ACID AS A REAGENT FOR ALKALINE PERMANGANATE

I. POTENTIOMETRIC DETERMINATION OF FORMATE

by

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Alkaline permanganate has become increasingly important in volumetric analysis for several determinations [1-7]. It has also been applied in the potentiometric determination of several metals *viz.* tellurium[1], lead[2], chromium and selenium (to be published later). The conventional reagent for the titration of alkaline permanganate is sodium formate. This was used by STAMM[3] and HEREDIA[4] for the back-titration of excess permanganate in strong alkaline media in the course of determining iodate, phosphite, arsenite, formate, cyanide[3], iodide, methyl alcohol, formaldehyde and formic acid[4]. The determination of the end-point in STAMM's procedure depends upon observing the pink permanganate colour through the dark green precipitate of $BaMnO_4$. The determination of formate by direct oxidation with permanganate[5] in alkaline solutions depends also on observing the pink colour through the brown MnO_2 precipitate, a process which is associated in both cases with some difficulty. Another difficulty inherent in the use of sodium formate as a reagent for the titration of permanganate is that the stability of its solutions varies with the purity of the constituents. Accordingly, it should be standardized[3] daily. JONES's method[6] for the determination of formate is liable to errors resulting from autodecomposition of permanganate (see below).

It was thought that these difficulties could be overcome by following the reactions potentiometrically and using formic acid as a reagent instead of sodium formate. The solutions of formic acid, which could be easily standardized with alkali, were found to be practically stable when suitably stored.

SINGH *et al.*[7] used formate for the potentiometric determination of excess permanganate, but neither these authors nor STAMM[3] gave the conditions under which a perfect quantitative titration could be performed. In this investigation the oxidation of formate with potassium permanganate and the reverse process, *i.e.* the reduction of permanganate with formic acid or formate, are studied under a variety of conditions *viz.* concentration of alkali and reactants. It is aimed to work out the best conditions favouring a quantitative reaction.

From free energy data[8] and using the relation[9]

$$\log K = \frac{n(E_1 - E_2)}{0.06} \text{ and } a = \frac{1}{K\,(n_1 + n_2)} \text{ at } 30^\circ\,\mathrm{C}$$

it is concluded that the reaction between permanganate and formate can take place quantitatively. The equilibrium constant K and the degree of completion a for the reaction taking place in weakly alkaline solutions and leading to the formation of MnO_2:

$$3\ HCO_2^- + 2\ MnO_4^- + OH^- = 3\ CO_3^{-2} + 2\ MnO_2 + 2\ H_2O$$

(for which E_1 the redox potential of the HCO_2^-/CO_3^{-2} system = —0.95 v and E_2 that of the MnO_4^-/MnO_2 system = 0.58[8] v, n, the number of faradays to complete the reaction = 6, z_1 and z_2 the valency changes of both reactants = 2 and 3 respectively) amount to 10^{-153} and $2.5 \cdot 10^{-31}$.

For the reaction taking place in strong alkaline media and leading to the formation of manganate

$$HCO_2^- + 2\ MnO_4^- + 3\ OH^- = CO_3^{-2} + 2\ MnO_4^{-2} + 2\ H_2O$$

(for which E_1 = —0.95 v and E_2 for the MnO^{-4}/MnO_4^{-2} system = 0.54[8], $n = 2$, z_1 and z_2 = 2 and 1 respectively), K and a amount to 10^{-51} and 10^{-17}.

EXPERIMENTAL

The titration device is similar to that previously described[9].

Preparation and standardization of solutions

a) Potassium permanganate solutions free from manganese dioxide were prepared according to the method of STAMM[3]. They were stored in brown coloured glass bottles and standardized with sodium oxalate "grade Analar"[9].

b) Formic acid solutions were prepared by the appropriate dilution of the concentrated acid "grade Merck". They were standardized by the aid of sodium hydroxide solutions free from carbonate and prestandardized with potassium hydrogen phthalate using in both cases phenolphthalein as indicator. The titrations were performed in presence of pure nitrogen. Sodium hydroxide solutions were prepared by diluting a carbonate-free 18N solution obtained from the Analar product with boiled-out twice distilled water in an atmosphere of pure nitrogen.

The normality of formic acid in the oxidation reaction will be double that obtained by neutralization. The solutions were checked from time to time and their normalities were found to be practically constant.

c) Sodium formate solutions were prepared by mixing a given volume of the checked formic acid solution with sodium hydroxide sufficient to neutralize the acid, and diluting the mixture in a measuring flask.

Solutions of varying concentrations were prepared from the well checked solutions by appropriate dilution.

In performing the titrations, 10 ml of formic acid were delivered to the titration vessel, 5*N* NaOH added, sufficient to neutralize the acid and to bring the alkalinity to that desired. The mixture was heated on a water bath to ∿ 80° C and then titrated with permanganate. In the back-titration a known volume of permanganate was mixed with the appropriate amount of alkali and titrated with formic acid or sodium formate solution. The titrations were performed both in the presence and absence of Ba^{+2} ions, the amount of the latter ions used was either the equivalent or twice the equivalent quantity necessary to precipitate all manganate formed by reduction.

RESULTS

Oxidation of sodium formate with potassium permanganate

In 0.1*N* NaOH, oxidation of formate with permanganate in the cold yields apparently a mixture of MnO_4^- and MnO_2. The reaction takes place very slowly needing ∿ 30 min for the attainment of equilibrium. In 1*N* NaOH the same phenomena manifest themselves, but the equilibrium needs 20 min after each addition. The titration curves under the above conditions are not characterized by inflections at the end-point. This is in conformity with the findings of HOLLUTA[11] that in the reaction between permanganate and formate in not too weakly alkaline solutions, the reduction of permanganate gave green MnO_4^{-2} which then reacted more slowly to give hydrated manganese dioxide.

Trials to accelerate the reaction by using as catalysts, Fe^{+3}, Cu^{+2} ions, HgO and ZnO did not lead to any result. Heating the formate solution in 0.1*N* NaOH to ∿ 80° C resulted in the reduction of MnO_4^- to MnO_2 but the reaction needed ∿ 15 min at the begining and ∿ 30 min at the end-point. The reaction was not sufficiently accelerated by Fe^{+3}, Cu^{+2}, Zn^{+2}, Hg^{+2} ions or HgO and ZnO. Fortunately, however, $Ag+$ ions possessed a considerable catalytic effect in hot solutions and equilibria were rapidly attained. As the catalytic activity decreased after some time, fresh amounts should be added from time to time. This difficulty could be overcome by mixing the silver nitrate solution with permanganate. The solutions used in the present titrations were ∿ 0.04*N* with respect to Ag^+ ions. Under these latter conditions the equilibria were attained after 2-5 min at the begining of the titration and only after 5-10 min at the end-point, depending upon the concentration of the formate solutions.

Sodium chloride also possessed a good catalytic activity such that the equilibria were attained after 8-10 min throughout till the end-point was reached.

It is noteworthy to remark that the potentiometric end-points, although corresponding to the exact amount of formic acid, as determined by neutralization, occurred 1-2% before the appearance of the pink colour in solution. This might be due to the difficulty of seeing the faint pink permanganate colour through the brown MnO_2 precipitate before an appreciable excess of permanganate has been added.

In Table I are shown some representative results of titrations, performed at ∿ 80° C in the presence of Ag^+ ions or NaCl. The results obtained are not far removed from the theoretical amounts present by more than 0.19% in the most dilute solution used. The curves representing these titrations are shown in Fig. 1. They are characterized by a gradual change in potential before the end-point is attained. At the end-point, characteristic inflections manifest themselves which are sharper in the concentrated solutions than in the dilute ones. Thus they amount to 70 mv per 0.1 ml of $KMnO_4$ when the formate used is $0.179N$ but decreases to only 14 mv when the solution is diluted to $2.295 \cdot 10^{-2}N$. At lower concentrations than the latter no inflection occurs.

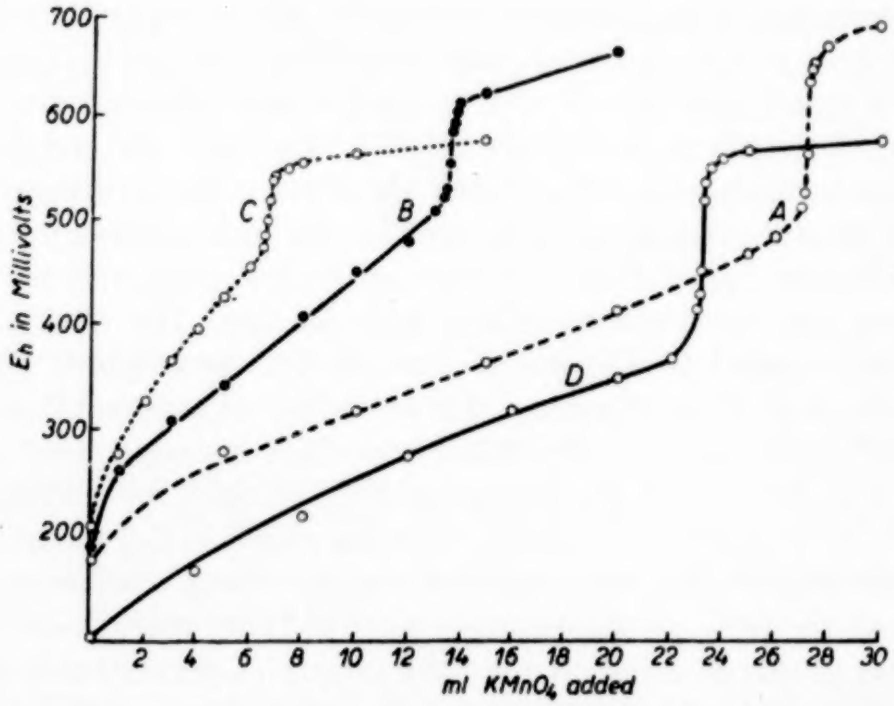

Fig. 1. Titration of 10 ml formate in $0.1N$ NaOH with $6.58 \cdot 10^{-2}N$ $KMnO_4$ at 80° C
A $1.79 \cdot 10^{-1}N$ formate, Ag^+ ion catalyst.
B $8.95 \cdot 10^{-2}N$ formate, Ag^+ ion catalyst.
C $4.475 \cdot 10^{-2}N$ formate, Ag^+ ion catalyst.
D $1.53 \cdot 10^{-1}N$ formate, NaCl catalyst.

TABLE I

TITRATION OF 10 ml FORMIC ACID IN $0.1N$ NaOH WITH $0.0658N$ $KMnO_4$, AT 80° C

Normality of formic acid	Max. inflecn. per 0.1 ml $KMnO_4$	Time for equil. (min)	mg formic acid present	mg formic acid found	error %
$1.79 \cdot 10^{-1}$ (Ag ion catalyst)	70	2—5	41.192	41.224	0.08
$8.95 \cdot 10^{-2}$,,	30	2—7	20.596	20.616	0.1
$4.475 \cdot 10^{-2}$,,	20	3—10	10.298	10.311	0.13
$2.295 \cdot 10^{-2}$,,	14	5—10	5.281	2.291	0.1
$1.53 \cdot 10^{-2}$,,	no inflection			—	—
$1.53 \cdot 10^{-1}$ (NaCl catalyst)	58	8—10	35.210	35.179	—0.09

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Reduction of potassium permanganate with formic acid and sodium formate in strong alkaline solutions

Reduction of permanganate in strong alkaline solutions with formate ions proceeds practically to the manganate state. This is favoured by the fact that at high alkali concentration, especially in presence of excess permanganate, reduction of the latter cannot proceed to MnO_2, manganate being only slowly reduced with formate. STAMM[3] showed that in concentrated alkali, oxidation of formate by MnO_4^{-2} was so slow that barium nitrate was able to remove MnO_4^{-2} ions quantitatively as $BaMnO_4$. From our results it becomes evident that even in the absence of Ba^{+2} ions reduction of MnO_4^- proceeds quantitatively to the manganate state.

In contradistinction to the oxidation of formate with permanganate the equilibria were attained more or less rapidly at room temperature (∿ 30° C). Using 0.02194*M* $KMnO_4$ and 0.1790*N* formic acid, the equilibria were attained after 1-2 min at the beginning of the titration but needed ∿ 5 min near the end-point, both in the presence and the absence of Ba^{+2} ions. On diluting the permanganate solution up to tenfold and the formate up to fourtyfold, the time necessary for the attainment of equilibrium varied from 2-3 min at the beginning and 7-10 min at the end of the reaction, the time increasing with dilution. The reaction could not, however, be accelerated by the use of HgO or ZnO as catalyst, although they were found capable of accelerating the oxidation of sodium plumbite through permanganate[2]. NaCl also did not produce any effect in accelerating the reaction. Catalysts such as Fe^{+3}, Cu^{+2}, Ni^{+2} ions could not be used, for, although they were recommended by STAMM[3] to be added near the end-point, they are oxidized in part to higher oxides[12]. We also observed that in strong alkaline solutions Ni^{+2} ions discharged the pink permanganate colour yielding manganate, and a black precipitate was produced different from the greenish hydrated nickel oxide. The interference of Ni^{+2} ions manifested itself by the occurrence of a sharp drop in potential on adding them to the permanganate solution.

In this reaction the potentiometric end-point, although corresponding exactly to the acid oxalate titration, occurred ∿ 2% after the disappearance of the pink permanganate colour.

As may be seen from the curves shown in Fig. 2, curve A, representing a titration performed in the presence of 0.1*N* NaOH, and in the absence of Ba^{+2} ions is not characterized by an inflection at the end-point. The inflection becomes apparent as the alkali concentration is made 0.5-2*N* in the presence of Ba^{+2} ions and 0.5-3.5*N* in the absence of these ions. In the presence of Ba^{+2} ions the inflections are sharper than in their absence, but in both cases they decrease, as may be seen from the results shown in Tables II and III by decreasing the concentration of the reactants. With $1.397 \cdot 10^{-3}$ or $7.985 \cdot 10^{-4}M$ $KMnO_4$ and $3.58 \cdot 10^{-3}N$ formate no inflection could be observed characterizing the end-point.

From the data shown in Tables II and III it is evident that good results can be obtained when the alkali concentration is 0.5-3N in the absence of Ba^{+2} ions and 0.5-1.5N in the presence of these ions when added in quantities equivalent, or double the equivalent, to the manganate formed. At higher alkalinities than those mentioned above the errors become appreciable on account of the autodecomposition of permanganate, especially in the presence of Ba^{+2} ions, as they precipitate $BaMnO_4$, thus aiding in shifting the equilibrium to manganate.

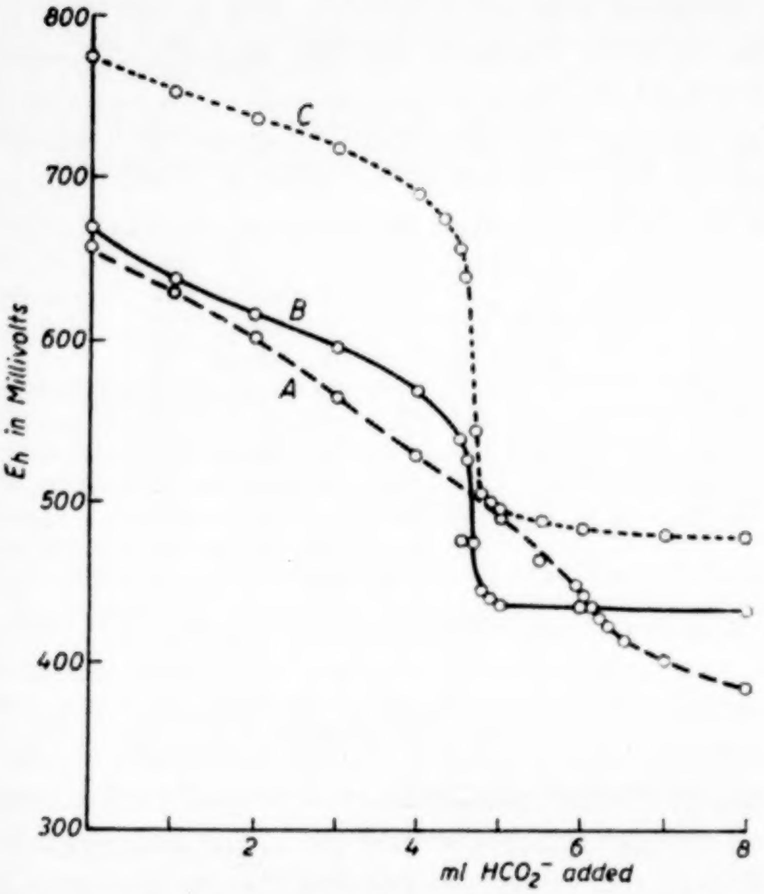

Fig. 2. A) Titration of 50 ml $2.194 \cdot 10^{-2} M$ $KMnO_4$ in $0.1 N$ NaOH in the absence of Ba^{+2} ions with $1.79 \cdot 10^{-1} N$ formate.

B) Titration of 10 ml $2.096 \cdot 10^{-2} M$ $KMnO_4$ in $22.55 N$ NaOH in the absence of Ba^{+2} ions with $4.475 \cdot 10^{-2} N$ formate.

C) Titration of 10 ml $2.096 \cdot 10^{-2} M$ $KMnO_4$ in $1 N$ NaOH in the presence of Ba^{+2} ions with $4.475 \cdot 10^{-2} N$ formate.

TABLE II

TITRATION OF $KMnO_4$ WITH FORMIC ACID OR FORMATE IN PRESENCE OF Ba^{+2} IONS AT 30° C

Mormality of $KMnO_4$ present	Alkali conc.	max. inflecn. per 0.1 ml formic	Molarity of formic acid or formate used	Molarity of $KMnO_4$ found	error %
50 ml $2.096 \cdot 10^{-2} M$	$0.5 N$	93	$1.79 \cdot 10^{-1} N$	$2.098 \cdot 10^{-2} M$	0.1
,, ,,	$0.7 N$	123	,,	$2.094 \cdot 10^{-2} M$	—0.1
,, ,,	$1.0 N$	95	,,	$2.096 \cdot 10^{-2} M$	nil
,, ,,	$1.5 N$	117	,,	$2.097 \cdot 10^{-2} M$	0.05
,, ,,	$2.0 N$	103	,,	$2.017 \cdot 10^{-2} M$	3.76
10 ml ,,	$1 N$	97	$4.475 \cdot 10^{-2} N$	$2.094 \cdot 10^{-2} M$	—0.1
25 ml $4.388 \cdot 10^{-3} M$	$1 N$	53	$8.95 \cdot 10^{-3} N$	$4.389 \cdot 10^{-3} M$	0.03
40 ml $2.194 \cdot 10^{-3} M$	$1 N$	14	$4.475 \cdot 10^{-3} N$	$2.193 \cdot 10^{-3} M$	—0.05
20 ml $1.597 \cdot 10^{-3} M$	$1 N$	no inflecn.	$3.58 \cdot 10^{-3} N$	—	—
40 ml $7.985 \cdot 10^{-4} M$	,,	,,	,,	—	—
50 ml $2.194 \cdot 10^{-2} M$ (50° C)	,,	80	$1.53 \cdot 10^{-1} N$	$1.944 \cdot 10^{-2} M$	—11.39

TABLE III

TITRATION OF $KMnO_4$ WITH FORMIC ACID OR FORMATE IN THE ABSENCE OF Ba^{+2} IONS AT 30° C

Molarity of $KMnO_4$	Alkali conc.	Max. inflecn. per 0.1 ml formic acid	Normality of formic acid	Molarity of $KMnO_4$ found	error %
10 ml $2.194 \cdot 10^{-2} M$	$0.1 N$	7	$1.79 \cdot 10^{-1} N$	—	—
,,	2	70	,,	$2.192 \cdot 10^{-2} M$	—0.09
25 ml ,,	0.5	37	$1.53 \cdot 10^{-1}$	$2.196 \cdot 10^{-2} M$	0.09
10 ml $2.096 \cdot 10^{-2} M$	1.5	50	$4.475 \cdot 10^{-2}$	$2.098 \cdot 10^{-2} M$	0.1
20 ml ,,	2	48	,,	$2.095 \cdot 10^{-2} M$	—0.06
10 ml ,,	2.5	53	,,	$2.097 \cdot 10^{-2} M$	0.05
20 ml $2.194 \cdot 10^{-2} M$	3	46	,,	$2.196 \cdot 10^{-2} M$	0.09
,, ,,	3.5	54	,,	$2.175 \cdot 10^{-2} M$	—0.86
10 ml ,,	2	38	$1.79 \cdot 10^{-2} N$	$2.195 \cdot 10^{-2} M$	0.09
50 ml ,, (50° C)	1.5	46	,,	$2.074 \cdot 10^{-2} M$	5.45

From the above results it is concluded that formic acid analysed with well-checked sodium hydroxide can be used satisfactorily in place of sodium formate for standardizing permanganate in alkaline media. Both in the presence of Ba^{+2} ions (0.5-1N NaOH) or absence of these ions (0.5-2.5N NaOH) reduction of permanganate proceeds in the cold, only to the manganate state. The results obtained by adjusting the alkali as required are comparable with those of the acid oxalate titration, without the necessity of performing blank experiments. As was stated before, the actual end-points do not coincide with those determined visually.

Accordingly the potentiometric formate method possesses more advantage over the visual method developed by STAMM[3] in the greater ease by which the exact end-point can be accurately determined.

In the method of JONES[6] there is the likelihood that autodecomposition can occur during the process of heating the mixture of formic acid with alkaline permanganate, because heating leads to considerable errors as may be seen from the results shown in Table IV.

TABLE IV

DETERMINATION OF FORMATE BY JONES METHOD

Molarity of $KMnO_4$	Alkali conc.	Heating period	Normality of formic acid used	Normality of formic acid found	error %
$2.194 \cdot 10^{-2}$	1.5	10 min	$1.530 \cdot 10^{-2} N$	$1.595 \cdot 10^{-2} N$	4.25
,,	2	,,	,,	$1.630 \cdot 10^{-2} N$	6.45
,,	2.5	,,	,,	$1.651 \cdot 10^{-2} N$	7.91

SUMMARY

Oxidation of formate with permanganate in alkaline solutions yields a mixture of MnO_4^{-2} and MnO_2. The reaction occurs slowly without an abrupt change in potential at the end-point. In 0.1N NaOH, at 80° C in the presence of Ag^+ ions or NaCl, the

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reaction is accelerated and yields MnO_2. The concentrations of formic acid obtained by oxidation with permanganate are comparable with those obtained by neutralization down to $2.295 \cdot 10^{-2} N$.

Reduction of permanganate in the presence of Ba^{+2} ions (alkalinity = 0.5 — 1.5N) or in the absence of Ba^+ ions (alkalinity = 0.5—2.5N), gave accurate results for the permanganate concentration comparable with the results of the acid oxalate method.

Formic acid is preferred to sodium formate on account of the greater stability of its solutions.

RÉSUMÉ

L'oxydation d'un formiate par le permanganate, en solution alcaline, donne un mélange de MnO_4^{-2} et MnO_2. La réaction se fait lentement sans changement brusque de potentiel au point final. La réaction est accélérée dans NaOH 0.1N à 80° C, en présence d'ions Ag^+ ou de NaCl, et donne du MnO_2. Les concentrations d'acide formique obtenues par oxydation avec le permanganate sont comparables à celles obtenues par neutralisation jusqu'à $2.295 \cdot 10^{-2} N$.

La réduction du permanganate en présence d'ions Ba^{+2} (alcalinité = 0.5—1.5N) ou en l'absence d' ions Ba^{+2} (alcalinité = 0.5—2.5N) a donné des résultats précis pour la concentration du permanganate, comparables aux résultats de la méthode à l'oxalate acide.

Les solutions d'acide formique sont préférables à celles du formiate de sodium à cause de leur plus grande stabilité.

ZUSAMMENFASSUNG

Die Oxydation von Formiat mit Permanganat in alkalische Lösung ergibt eine Mischung von MnO_4^{-2} und MnO_2. Die Reaktion geht langsam vonstatten, ohne eine schnelle Potentialänderung im Endpunkt. Die Reaktion wird bei einer Temperatur von 80° C in 0.1N alkalischer Lösung in Gegenwart von Ag^+-Ionen oder von NaCl beschleunigt, wobei MnO_2 gebildet wird.

Die durch die Permanganat-Oxydation erreichten Ameisensäure-Konzentrationen sind denjenigen vergleichbar, die durch Neutralisation mit Alkali (bis $2.295 \cdot 10^{-2} N$) erhalten werden.

Die Reduktion von Permanganat in Gegenwart von Ba^{+2}-Ionen (Alkalinität = 0.5—1.5N) oder in Abwesenheit von Ba^{+2}-Ionen (Alkalinität = 0.5—2.5N) ergab für die Permanganat-Konzentration genaue Resultate, welche mit den, durch Titration mit saurem Oxalat erhaltenen, vergleichbar sind. Ameisensäure ist dem Natriumformiat wegen der grösseren Beständigkeit seiner Lösungen vorzuziehen.

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BÜCHERBESPRECHUNGEN

Makromolekulare Chemie, ein Lehr- und Handbuch für Chemiker und Biologen von K. H. MEYER UND H. MARK. 3. Auflage, wenig verändert von K. H. MEYER unter Mitwirkung von A. J. A. VAN DER WIJK. xxiv und 1026 Seiten, 229 Abbildungen. Akademische Verlagsgesellschaft Geest & Portig K.-G., Leipzig 1953, Preis D.M. 58,—.

Ein Spezialwerk, das in 3. Auflage erscheint, empfiehlt sich von selbst. Daneben stellt diese Ausgabe der „Makromolekularen Chemie" das Vermächtnis eines bedeutenden Forschers an uns dar; während KURT HANS MEYER diese neue Auflage bearbeitete, nahm ihm der Tod die Feder aus der Hand. Trotzdem konnte durch dankenswerte Unterstützung früherer Mitarbeiter die Auflage noch einmal in wenig veränderter Form gegenüber der zweiten erscheinen.

Das Werk gibt einen Überblick über die makromolekulare Chemie in Wissenschaft und Technik in folgenden Abschnitten: A. Bindungskräfte und Molekülbau, B. Die physikalische und physikalisch-chemische Untersuchung der Hochpolymeren, C. Anorganische Hochpolymere, D. Hochpolymere Kohlenwasserstoffe und ihre Derivate, E. Polymere Äther, Ester Sulfide usw., F. Die Cellulose und ihre Derivate, G. Begleitstoffe der Cellulose; pflanzliche und tierische Polysaccharide, H. Die Proteine, J. Das Verhalten der Hochpolymeren in Lösung, K. Elastizität, Viskosität und Plastizität der Hochpolymeren, L. Filme, Folien und Membranen, M. Der molekulare Feinbau der lebenden Substanz. Ein Autoren- und Sachregister beschließt den Band.

Die Bedeutung des Werkes liegt in der kritischen Gesamtschau dieses in den letzten Jahren zu großem Umfange angewachsenen Gebiet durch eine Persönlichkeit, die die ganze Entwicklung miterlebt und mitgetragen hat. Demgegenüber fallen die wenigen einseitigen Stellungnahmen, die sich in dem Buch finden und die zum Teil durch unsere heutige Kenntnis sogar schon widerlegt sind, kaum in Betracht. Bedauerlicher ist, daß der Verfasser nurmehhr vereinzelt die Literatur bis 1950 berücksichtigen konnte, wodurch besonders der deutschsprachige Anteil an der Entwicklung zu kurz gekommen ist.

Trotzdem kann auch die 3. Auflage dieses Lehr- und Handbuches der makromolekularen Chemie dank seiner Geschlossenheit und Ausführlichkeit genau so empfohlen werden wie die früheren. Der Leser wird darin sowohl eine tragfähige Einführung in das Gesamtgebiet als auch zuverlässige Beratung in Einzelfragen finden.

F. PATAT (Hannover)

Organische Fällungsmittel in der quantitativen Analyse, von W. PRODINGER. 3. Auflage Ferdinrnd Enke Verlag, Stuttgart. xv und 232 Seiten, 3 Abbildungen, 9 Tabellen. Gehftet 32 D.M. Ganzleinen 34 D.M.

Der neue Prodinger, nunmehr bereits in der dritten Auflage erschienen, ist sicher ein Bedürfnis für den analytisch arbeitenden Chemiker, wie schon dadurch dokumentiert wird, dass bereits die dritte Auflage notwendig gewordewen ist Im Gensatz zu den beiden früheren Auflagen erscheint das Werk zweckmässig erwnitert, wodurch es den Anforderungen der modernen Fällungsanalyse vollkommen gerecht wird. Es werden mit wenigen Ausnahmen fast sämtliche gebräuchlichen organischen, für die Gravimetrie bedeutsamen Reagenzien besprochen, wobei auch eventuelle hiemit verknüpfte massanalytische und kolorimetrische Bestimmungsformen Berücksichtigung finden. Hiedurch erweist sich das Werk nicht nur für die Makroanalyse, sondern auch für die Mikroanalyse als sehr brauchbar, da die meisten der angeführten Verfahren auch im Mikromasstab durchführbar sind. In diesem Sinne ist das Buch als wertvolle Bereicherung der Literatur dieser Richtung zu bezeichnen.

G. GORBACH (Graz)

STRUCTURE AND BEHAVIOR OF ORGANIC ANALYTICAL REAGENTS

VI. HEATS AND ENTROPIES OF FORMATION OF SEVERAL DIVALENT METAL CHELATES OF 2- AND 4-METHYL-8-HYDROXYQUINOLINE[1]

by

W. D. JOHNSTON[2] AND H. FREISER

Contribution of the Department of Chemistry, University of Pittsburgh, Pa. (U.S.A.)

It has been well established that any substitution in the 2-position of 8-hydroxyquinoline prevents the precipitation of an aluminum complex. This effect was first noted by MERRITT AND WALKER[3] in the case of 2-methyl-8-hydroxyquinoline. IRVING[4] and co-workers established the general nature of this effect by a study of the analytical behavior of 2,4-dimethyl- and 2-phenyl-8-hydroxyquinoline as well as 1-hydroxyacridine and 9-hydroxy-1,2,3,4-tetrahydroacridine. They reasoned that this effect was due to the steric hindrance provided by the group in the 2-position. ALBERT[5] has noted that any substituent in the 2-position of 8-hydroxyquinoline lowered its antibacterial action.

In a previous paper the authors[6] have reported formation constants for a number of metal chelates of 8-hydroxyquinoline and 2-methyl-8-hydroxyquinoline. It was found that the chelates of 2-methyl-8-hydroxyquinoline were slightly less stable than those of 8-hydroxyquinoline. However, the nickel(II) chelate of 2-methyl-8-hydroxyquinoline was considerably less stable than the corresponding chelate of 8-hydroxyquinoline. This unusual effect was so pronounced that the usual metal sequence Cu(II) $>$ Ni(II) $>$ Co(II), Zn(II) $>$ Mn(II) was violated in that the nickel(II) chelate was found to be less stable than those of cobalt(II) and zinc(II).

In order to explore these effects in greater detail it was thought appropriate to determine the $\triangle H$ and $\triangle S$ values for the formation of chelates of 2-methyl-8-hydroxyquinoline. The $\triangle F$, $\triangle H$ and $\triangle S$ values for the chelation reactions of 4-methyl-8-hydroxyquinoline were obtained as a comparison. Formation constants of chelates of 2-phenyl-8-hydroxyquinoline were also determined to extend our study of sterically hindered 8-hydroxyquinolines.

EXPERIMENTAL

Materials. The method of preparation of 2-methyl-8-hydroxyquinoline was described previously[6]. 4-Methyl-8-hydroxyquinoline was prepared from methyl vinyl ketone and *o*-aminophenol by the DOEBNER-VON MILLER reaction[7]. After recrystallization from alcohol and water it melted at 140-142° (reported[7] 141°). 2-Phenyl-8-hydroxyquinoline was prepared by the method of GILMAN from 8-hydroxyquinoline and phenyllithium[7]. After decolorization with charcoal and recrystallization from alcohol and water it melted at 58.5-59° (reported[7] 59°).

The method of purification of dioxane and the procedures used in standardizing metal perchlorate solutions have been previously described[8].

Apparatus and Procedure. The titration apparatus and procedure have been previously described[8]. Temperature was controlled at 0.7 ± 0.1° C by immersing the titration apparatus in a water-ice bath. At 25 and 40° C temperature was controlled to ± 0.2° C by circulating water from a constant temperature bath through the water jacket of the titration vessel. An atmosphere of nitrogen, previously saturated with a 50% water-dioxane mixture at the appropriate temperature, was maintained over the titration mixture.

Calculations. The CALVIN-BJERRUM method of determining stability constants was applied as previously described[8]. As mentioned in paper IV, it has been the general practice in this type of study to take pH meter readings as an accurate indication of hydrogen ion concentration. In many cases this is a very satisfactory approximation but where more accurate formation constants are required, such as in the determination of temperature coefficients of stability constants, it becomes necessary to make small corrections. These are particularly important at the higher temperatures. By comparison of pH meter readings with theoretically calculated hydrogen ion concentrations, correction factors were determined which were independent of pH but which varied with temperature. Thus it was possible to correct pH meter readings to hydrogen ion concentrations by adding respectively 0.01, 0.07, and 0.14 to the pH meter reading at 0.7° C, 25° C and 40° C.

In order to be strictly comparable, the formation and acid dissociation constants at 25° C for 2-methyl-8-hydroxyquinoline chelates were redetermined at the conditions of the present work. This involved slightly larger concentrations of the reacting species. This factor combined with the correction to pH readings which were not previously applied gives stability constants that are somewhat lower than those previously reported.

Results. Table I lists the stepwise formation constants for chelates of 2-methyl- and 4-methyl-8-hydroxyquinoline determined at 0.7, 25 and 40° C. The free energies of formation at these temperatures are also listed. The free energy terms refer to complete chelate formation and are calculated from the values given for 2 log K_{av} ($K_{av} = \sqrt{K_1K_2}$). For comparison, the formation constants for chelates of 2-phenyl-8-hydroquinoline are included. The acid dissociation constants of the three reagents are also listed. All data were obtained in pH regions which previously had been shown to be free of metal hydrolysis[8]. Hydrolysis of the metal ion or precipitation of the metal chelate precluded precise calculation of stability constants in a number of instances. In some of these cases calculated or extrapolated values are listed parenthetically.

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The stability data listed in Table I were used in calculating $\triangle H$ of complete chelation by measuring the slopes of the curves shown in Figures 1a, b, and c. The $\triangle S$ values of the formation reactions were calculated from the $\triangle F$ and $\triangle H$ values. The heats and entropies of chelation are given in Table II.

TABLE I

SUMMARY OF CHELATE FORMATION CONSTANTS

4-Methyl-8-hydroxyquinoline	Temp. °C	log K_1	log K_2	2 log K_{av}	—$\triangle F$ kcal.
Cu(II)	0.7	—	14.32	(29.86)	37.33
Ni(II)	0.7	12.36	—	(23.94)	29.93
Co(II)	0.7	11.29	10.08	21.30	26.63
Zn(II)	0.7	11.25	(10.28)	21.40	26.76
Mn(II)	0.7	8.63	(7.60)	16.22	20.28
Cu(II)	25	—	13.52	(27.54)	37.58
Ni(II)	25	11.57	(10.72)	22.28	30.40
Co(II)	25	10.55	(9.45)	20.00	27.29
Zn(II)	25	10.67	(9.57)	20.24	27.62
Mn(II)	25	8.31	7.24	15.50	21.15
Pb(II)	25	11.11	8.13	18.76	25.60
Cd(II)	25	9.44	—	(17.20)	23.47
Mg(II)	25	6.45	5.46	11.90	16.24
Cu(II)	40	—	12.88	(26.46)	37.92
Ni(II)	40	11.15	10.17	21.34	30.58
Co(II)	40	10.22	—	(19.28)	27.63
Zn(II)	40	10.25	(9.19)	19.44	27.86
Mn(II)	40	8.12	(6.94)	15.06	21.58

2-Methyl-8-hydroxyquinoline	Temp. °C	log K_1	log K_2	2 log K_{av}	—$\triangle F$ kcal.
Cu(II)	0.7	12.94	11.74	24.74	30.93
Ni(II)	0.7	9.67	8.71	18.44	23.06
Co(II)	0.7	9.97	9.17	19.16	23.96
Zn(II)	0.7	10.07	(9.27)	19.32	24.16
Mn(II)	0.7	7.75	(6.85)	14.56	18.20
Cu(II)	25	12.48	11.32	23.84	32.53
Ni(II)	25	9.41	8.35	17.84	24.34
Co(II)	25	9.63	8.87	18.44	25.16
Zn(II)	25	9.82	—	18.72	25.54
Mn(II)	25	7.44	6.55	14.00	19.10
Pb(II)	25	10.30	(8.20)	18.50	25.24
Cd(II)	25	9.00	—	(16.60)	22.65
Mg(II)	25	5.24	4.48	9.72	13.26
Ce(III)	25	7.71	—	—	—
Cu(II)	40	12.12	10.82	23.00	32.96
Ni(II)	40	9.07	8.22	17.36	24.88
Co(II)	40	9.37	8.74	18.14	26.00
Zn(II)	40	9.47	—	(18.28)	26.20
Mn(II)	40	7.40	6.50	13.90	19.92

TABLE I (Continued)

2-Phenyl-8-hydroxyquinoline	Temp. °C	log K_1	log K_2	2 log K_{av}	$-\triangle F$ kcal.
Cu(II)	25	11.40	10.89	22.26	30.37
Ni(II)	25	7.57	6.93	14.50	19.78
Co(II)	25	(7.75)	—	—	—
Zn(II)	25	9.00	8.52	17.54	23.93
Mn(II)	25	(6.22)	—	—	—

SUMMARY OF ACID DISSOCIATION CONSTANTS

	Temp.	pK_{NH}	pK_{OH}	$\triangle F_{NH}$ kcal.	$\triangle F_{OH}$ kcal.
4-Methyl-8-hydroxyquinoline	0.7	5.18	12.22	6.48	15.27
4-Methyl-8-hydroxyquinoline	25	4.67	11.62	6.37	15.85
4-Methyl-8-hydroxyquinoline	40	4.45	11.31	6.38	16.20
2-Methyl-8-hydroxyquinoline	0.7	5.00	12.18	6.25	15.23
2-Methyl-8-hydroxyquinoline	25	4.58	11.71	6.24	15.98
2-Methyl-8-hydroxyquinoline	40	4.31	11.44	6.18	16.39
2-Phenyl-8-hydroxyquinoline	25	2.07	11.87	2.83	16.19

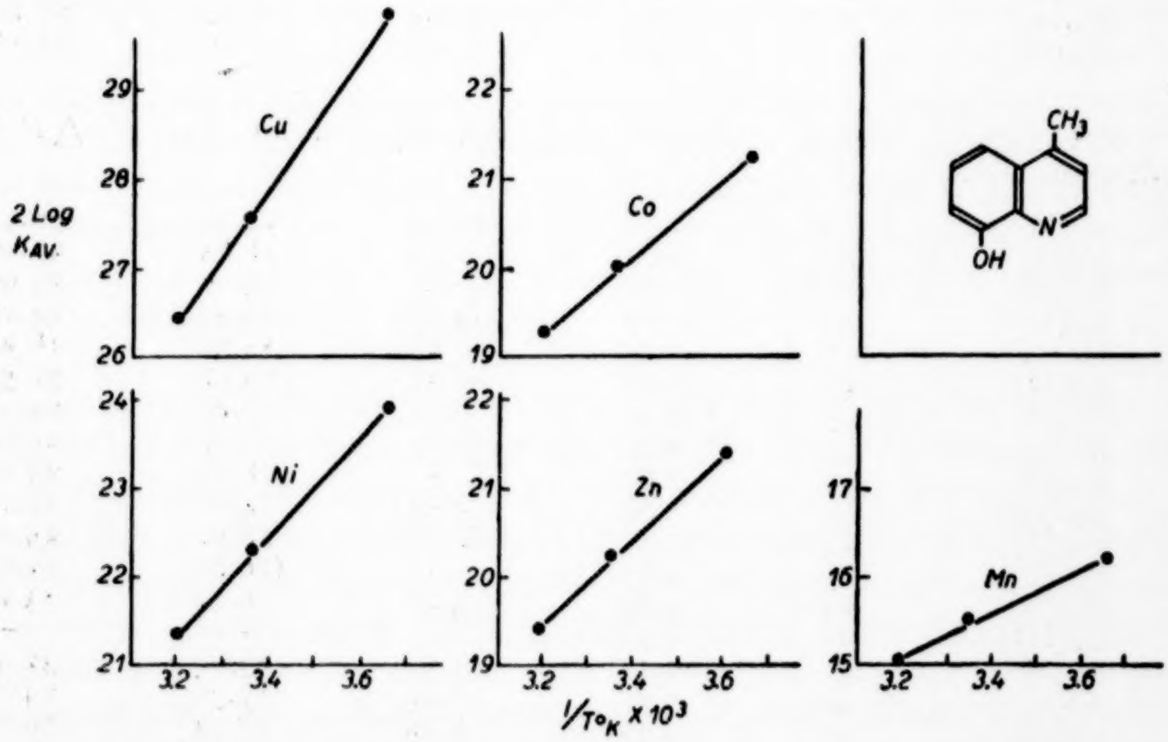

Fig. 1a. Temperature dependence of chelate stability, 4-methyl-8-hydroxyquinoline.

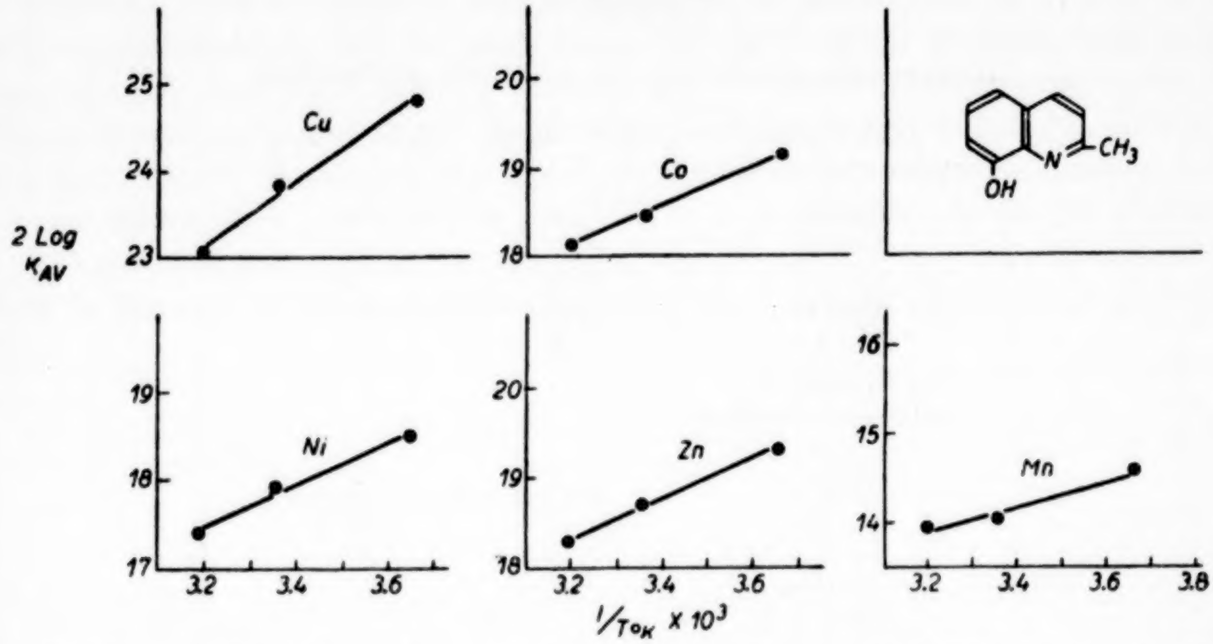

Fig. 1b. Temperature dependence of chelate stability, 2-methyl-8-hydroxyquinoline.

The constants reported in Table II are not thermodynamic constants in that no activity coefficients have been employed. The low ionic strengths encountered (0.005) minimize the necessity of such a correction when using the stability data at one temperature for purposes of comparison. The neglect of activity coefficients when heats and entropies of reactions are calculated results in errors only insofar as the neglected activity coefficients vary with temperature. It is estimated that this variation results in errors which are negligible compared with normal experimental errors.

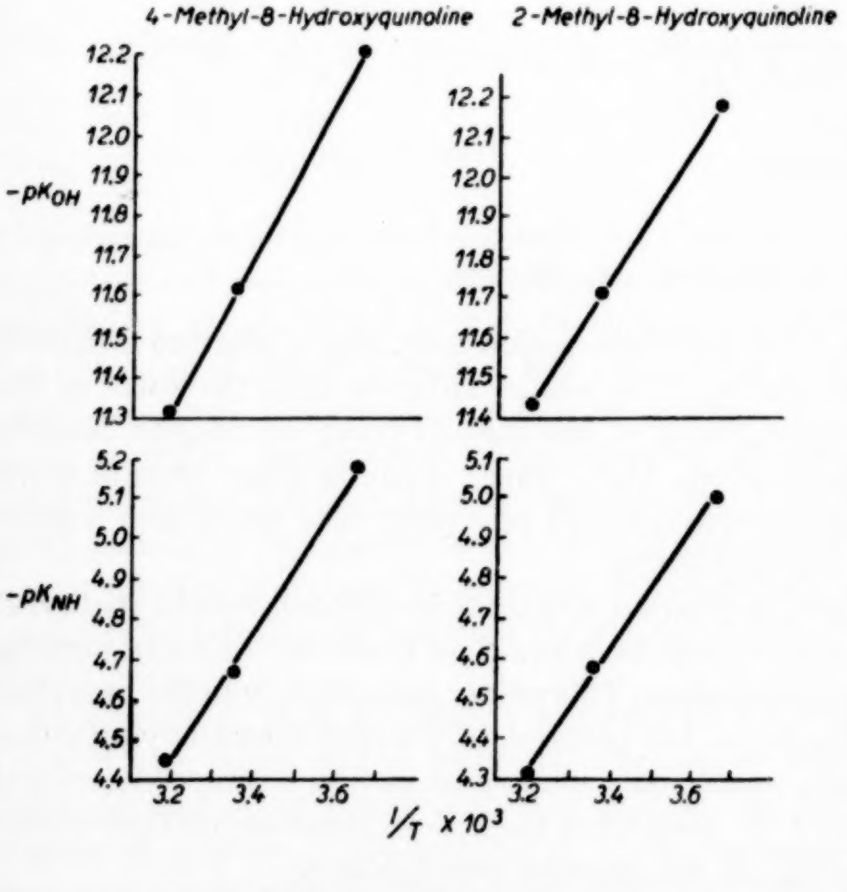

Fig. 1c. Temperature dependence of reagent ionization constants.

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TABLE II

HEATS AND ENTROPIES OF CHELATE FORMATION

4-Methyl-8-hydroxyquinoline	$-\Delta H$ kcal.	ΔS e. u.
Cu(II)	34.1	12.
Ni(II)	26.0	15.
Co(II)	20.3	23.
Zn(II)	19.6	26.
Mn(II)	11.6	32.
2-Methyl-8-hydroxyquinoline		
Cu(II)	17.3	50.
Ni(II)	10.7	46.
Co(II)	10.3	50.
Zn(II)	10.3	51.
Mn(II)	6.6	42.
4-Methyl-8-hydroxyquinoline		
imino H*	7.1	—2.
phenolic H*	9.1	23.
2-Methyl-8-hydroxyquinoline		
imino H*	6.9	—2.
phenolic H*	7.5	28.

(*) expressed as formation constants

$$K_{NH} = \frac{(H_2R^+)}{(H^+)(HR)} \qquad K_{OH} = \frac{HR}{(H^+)(R^-)}$$

DISCUSSION OF RESULTS

As can be seen from Table I the acid dissociation constants of the two methyl-8-hydroxyquinolines are very similar. This would indicate that the total of the inductive and hyperconjugative effects of the methyl group on reagent basicity is nearly independent of its position. Thus, unless there is some type of steric hindrance involved, these two reagents would be expected to react with a given metal to form chelates of equal stability.

Table I shows that the overall formation constants for all chelates of 2-methyl-8-hydroxyquinoline are from 1.5 to 5 log units less than those for the corresponding chelates of 4-methyl-8-hydroxyquinoline. This points immediately to the operation of some type of steric hindrance in the chelates of 2-mehyl-8-hydroxyquinoline. This stability decrease is more graphically illustrated in Fig. 2 where the overall formation constants at 25° C of the chelates of the two reagents are plotted against the second ionization potential of the gaseous metal atom.

Fig. 2 also points out the previously reported fact that the stability of the nickel(II) chelate of 2-methyl-8-hydroxyquinoline is considerably less than would

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be expected. Such an effect is also found in the nickel(II) chelate of 2-phenyl-8-hydroxyquinoline. In fact in both cases the usual metal stability sequence is violated such that the nickel(II) chelates are less stable than the corresponding cobalt(II) and zinc(II) chelates. Work in this laboratory has definitely established that this relative decrease in the stability of a nickel(II) chelate is always found in cases where steric hindrance is possible. In a previous report on the stabilities of chelates of dimethylglyoxime the usual metal stability sequence is adhered to while in the case of its O-monomethyl ether the hindered metal order is found[1].

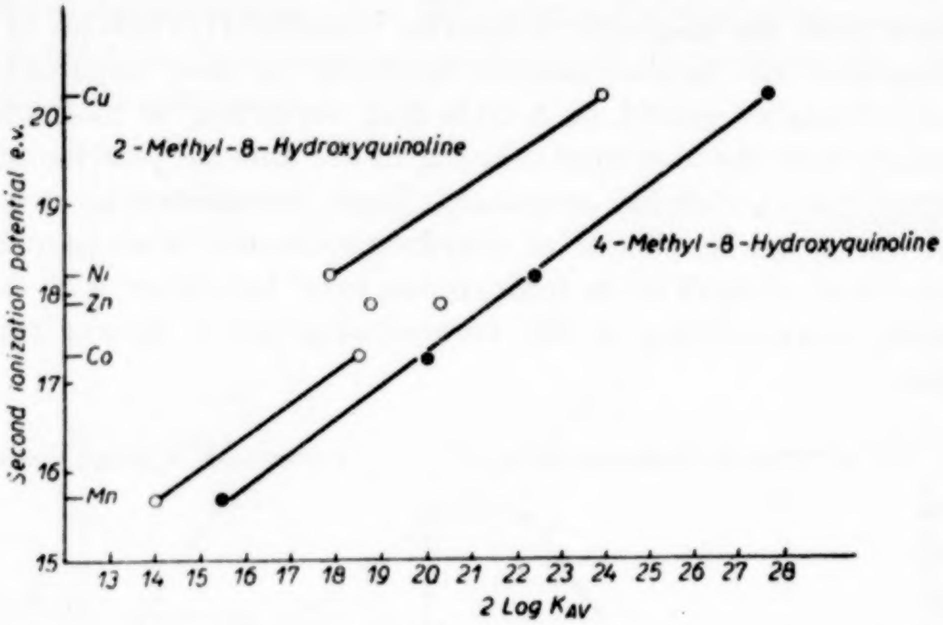
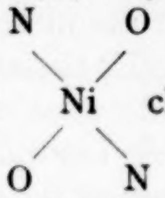


Fig. 2.

This unusual order has also been found in chelates of 2-(*o*-hydroxyphenyl)-benzothiazoline and 2-(*o*-hydroxyphenyl)-benzoxazole[9]. In every case when there is a substituent group on the carbon in alpha position to the heterocyclic nitrogen the hindered stability sequence has been found. This effect is still not clearly understood but it seems reasonable to assume that the tendency of nickel(II) to form planar complexes is being hindered, giving rise to either a strained or distorted planar configuration or possibly even a tetrahedron. A molecular model of the nickel(II) chelate of 2-methyl-8-hydroxyquinoline shows that a symmetrical planar configuration would be nearly impossible to attain since there would be considerable interference between the methyl group of one reagent and the oxygen of the other.

This point of view is difficult to reconcile with the findings of MELLOR AND CRAIG[10] who reported the nickel(II) chelate of 8-hydroxyquinoline to be paramagnetic and hence presumably tetrahedral. On the other hand, the nickel(II) chelate of *o*-aminophenol was found to be diamagnetic and therefore of square coplanar configuration. From these magnetic data one would predict that the bonds in the *o*-aminophenol chelate would be stronger, giving rise to greater chelate stability, than those of the 8-hydroxyquinoline chelate. Actually the reverse has been found to be true[6,11]. Further, the nickel(II) 8-hydroxyquinolinate was exceptional in that it was the only one of the class  chelates (where O originally formed part of a phenolic hydroxide group) which displayed paramagnetism in the MELLOR AND CRAIG investigation.

If we assume that the magnetic properties in nickel(II) chelates of alkylated 8-hydroxyquinolines are similar, another anomaly becomes apparent. The fact that the nickel chelates should be tetrahedral, according to magnetic data, is not in agreement with the argument relating to the unusual position of nickel(II) in the hindered metal stability sequence. These inconsistencies together with the fact that the nickel(II) chelate of 8-hydroxyquinoline is an exception to the MELLOR AND CRAIG classification indicate the need for either a re-examination of the magnetic susceptibility of this compound or the re-interpretation of the magnetic data.

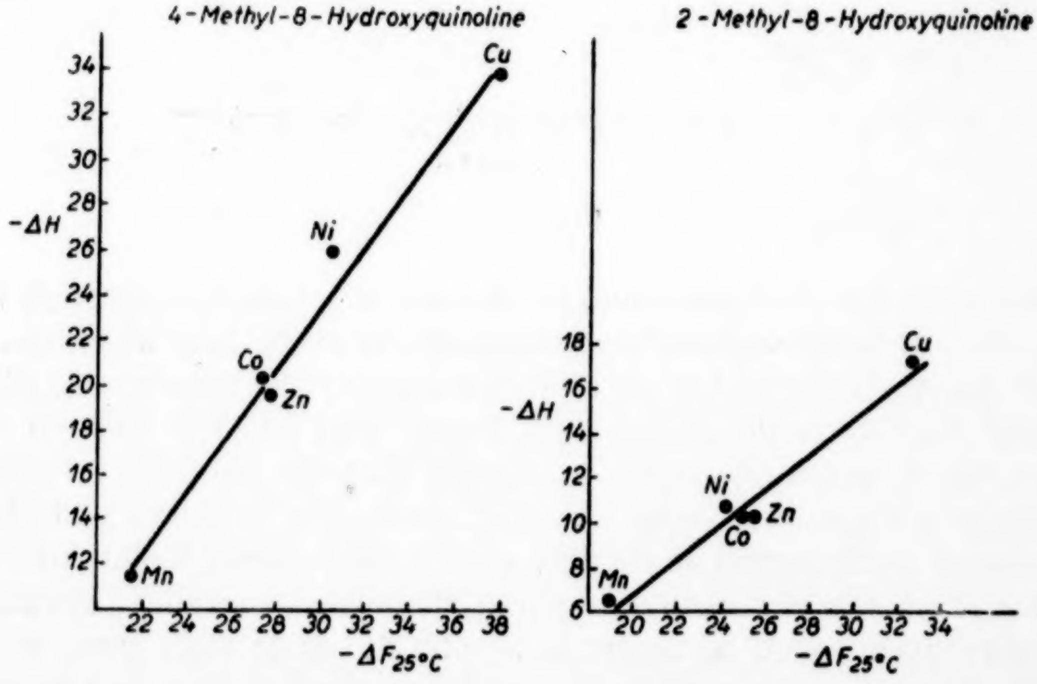


Fig. 3.

Fig. 3 shows a plot of $\triangle F$ *vs* $\triangle H$ for the chelates of the two reagents. It can be seen that these curves are roughly linear. This is to say that the entropy changes of the reactions have caused no unusual effects within the chelates of a given reagent. It is reasonable to assume that this will generally be true. That is, the entropy of a series of chelation reactions with a given reagent will either be roughly constant or will vary regularly. This accounts for the widespread success of the log K_{vs} second ionization potential graphs. Each time this relationship is used it is implicitly assumed that only bond strength or $\triangle H$ is involved. Since the second ionization potential may be taken as a rough estimation of the average electron attracting power of a divalent metal ion it will also be a measure of the attracting power of that divalent metal ion for a source of electrons such as are found in the chelate ligand groups. Hence it is more nearly related to bond energy and $\triangle H$ of chelation than to $\triangle F$ as measured by the log of the chelate formation constant. It should also be noted that since in many cases changes in $\triangle H$ are accompanied by opposing changes in $\triangle S$, $\triangle H$ should be a more sensitive index of bond strength than $\triangle F$. Fig. 4 shows a plot of the second ionization potential of the gaseous metal atom against $\triangle H$ of chelation. As can be seen the relationship is satisfactory.

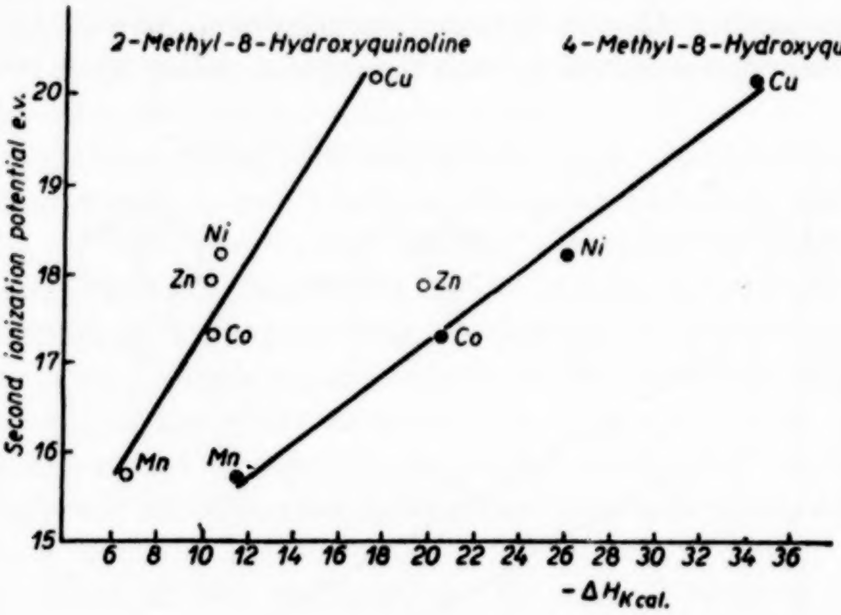


Fig. 4.

Very few determinations of $\triangle H$ have been published for neutral chelate species. However, a number of such investigations have been made on the metal ammine type of complexes. Of particular interest are the very comprehensive studies by JONASSEN *et al.*[12] on complexes of diethylenetriamine and triethylenetetramine. The heat of reaction sequence for the complexes of both of these reagents follow the normal stability order rather closely. MCINTYRE[13] gives a rather complete compilation of the thermodynamic functions for metal ammine formation. In practically all cases listed the heats of reaction for complexes of a given reagent follow the normal metal stability sequence.

A comparison of the $\triangle H$ values listed in Table II points out the importance of steric hindrance in all chelates of 2-methyl-8-hydroxyquinoline. In all cases the heats of chelation for chelates of 2-methyl-8-hydroxyquinoline are only about half that found associated with the respective chelates of the 4-methyl compound.

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This points to a very large decrease in bond strength due to the hindrance of the 2-methyl group. It is reasonable to assume that the presence of the 2-methyl group prevents the close approach of the two reagent molecules around the metal atom regardless of the preferred configuration and thus causes the chelate bonds considerable strain. Therefore, one might reasonably expect the magnitude of the steric effect to increase with decreasing metal size. For this purpose, the thermodynamic functions of the exchange reaction,

$$MQ_2 + 2L^- \rightleftarrows ML_2 + 2Q^-$$

where Q^- and L^- are the anions of 2-methyl- and 4-methyl-8-hydroxyquinoline, respectively, were plotted against the divalent crystal radii of the metals involved. Although there are a number of conflicting sets of values of crystal radii, those of PAULING[14] were used mainly because these are the values used also by POWELL AND LATIMER[15] in similar thermodynamic calculations. As can be seen from Fig. 5 the $T\triangle S$ term varies regularly with the crystal radius while with $\triangle F$ and

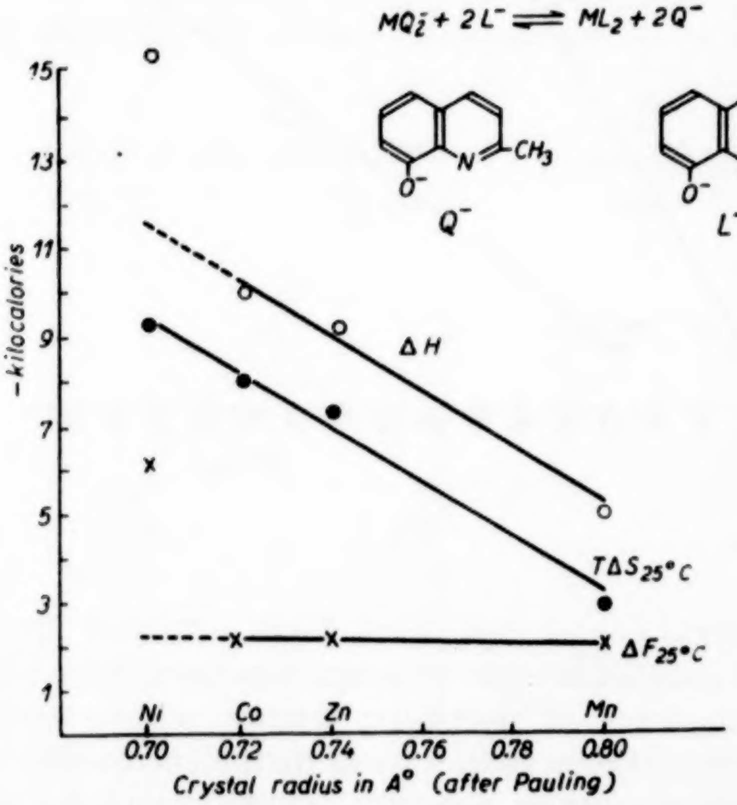

Fig. 5. Comparison of thermodynamic functions of alkylated 8-hydroxyquinoline chelates.

$\triangle H$ there are sharp discontinuties in the case of nickel(II). In agreement with our expectations, the exchange reactions become more exothermic as the crystal radii decrease. It appears that in the case of nickel(II) a minimum radius has been reached and steric hindrance is excessive. This helps to explain the decreased stability that has been observed in the case of hindered nickel(II) chelates.

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The relatively large entropy increase associated with the formation of chelates of 2-methyl-8-hydroxyquinoline was rather surprising but not unprecedented. FRANK AND EVANS[16] have interpreted the following data in terms of steric hindrance and the structure-making influence on water of the reagents and complexes.

$Ni^{+2}(aq.) + 6NH_3(aq.) \rightleftharpoons [Ni(NH_3)_6]^{+2}(aq.)$; $\triangle H$ = -19 kcal., $\triangle S$ = -22 e. u.

$Ni^{+2}(aq.) + 6CH_3NH_2(aq.) \rightleftharpoons [Ni(CH_3NH_2)_6]^{+2}$ (aq.); $\triangle H$ = +9.7 kcal., $\triangle S$ = +73 e. u.

Although the complexes formed are of about equal stability spatial requirements prevent the close approach of the six methylamines about the nickel(II) ion according to arguments presented by CALVIN and discussed by FRANK AND EVANS. This easily accounts for the more positive heat of reaction in the hindered case. This is in qualitative agreement with the heat effects presented in this paper. The relatively large positive entropy term in the hindered reaction above is also in agreement with the results presented here.

The interpretations of these entropy effects are rather difficult. FRANK AND EVANS attributed only a small part of the greater entropy of formation of the $[Ni(CH_3NH_2)_6]^{+2}$ to its greater size relative to that of the $[Ni(NH_3)_6]^{+2}$ complex. They speculated that the larger part of the entropy contribution might be due to the imposition of iceberg-forming tendencies on the methylamine molecule by the methyl group which would lower its partial molal entropy compared with that of ammonia. If the water structure breaking tendencies of both complexes were similar this would account for the greater entropy of reaction in the second case. Although not strictly comparable, the thermodynamic data of SPIKE AND PARRY[17] which describe the formation of $[Cd(NH_3)_4]^{+2}$ and $[Cd(CH_3NH_2)_4]^{+2}$ tend to cast doubt on this explanation. No steric hindrance was found in the cadmium(II) complexes as evidenced by similar values of $\triangle H$. Of greater importance is the fact that the $\triangle S$ values of SPIKE AND PARRY do not reflect a trend similar to that reported by FRANK AND EVANS.

The large difference in the $\triangle S$ values for the formation of 2-methyl- and 4-methyl-8-hydroxyquinoline chelates is probably best explained by noting that methyl groups in the 2-positions of a chelate of 8-hydroxyquinoline might be able to partially shield the polar oxygen, nitrogen, and metal atoms while no such shielding would be possible in the corresponding 4-methyl-chelate. Shielding would reduce the attractive forces between the solvent molecules and these polar atoms and allow the solvent much greater freedom by virtually eliminating any remnant of a first coordination sphere.

An interesting alternative explanation can be sought in the inverse relation of $-\triangle H$ and $\triangle S$. In the case of the exchange reactions mentioned above and also in the case of formation of 4-methyl-8-hydroxyquinoline chelates there seems to be a linear inverse relation between $-\triangle H$ and $\triangle S$. It is probable that as the bond strength decreases, the freedom of motion involving the atoms so bonded, increases. This increased freedom of motion may well result in a significant entropy increase. This relationship involving intramolecular forces may be considered analogous to that of BARCLAY AND BUTLER[18] (linear relation of $\triangle H$ and $\triangle S$ of vaporization of certain non-ionized solutes) in which intermolecular, non-valence, forces are involved.

It would be interesting to study the entropies and heats of chelation for chelates of 7-methyl-8-hydroxyquinoline. IRVING[4] reports that aluminum precipitation takes place with this reagent which indicates that steric hindrance is probably absent. Further he has found that this reagent exhibits greater average sensitivity than other substituted 8-hydroxyquinolines. It is quite possible that this reagent combines the favorable qualities of both 2-methyl- and 4-methyl-8-hydroxyquinoline. Due to the unhindered configuration of its chelates it probably involves heats of chelate formation of the order of those exhibited by 4-methyl-8-hydroxyquinoine. Further, due to the shielding effect of the 7-methyl group the entropy of reaction might be rather high. These two effects should result in the increased stability which may be inferred from IRVING's sensitivity data.

ACKNOWLEDGEMENT

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SUMMARY

The CALVIN-BJERRUM titration technique for the determination of chelate formation constants has been applied to the Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) chelates of 2- and 4-methyl-8-hydroxyquinoline. Measurements were made at several temperatures in order to evaluate $\triangle H$ and $\triangle S$ values of chelation. The results obtained were interpreted in terms of steric hindrance of the 2-methyl group. In all cases the heats of formation of the chelates of 2-methyl-8-hydroxyquinoline were remarkably more positive than those for the corresponding chelates of 4-methyl-8-hydroxyquinoline. This large difference in the strengths of the metal-chelate bonds is apparently due to the hindrance of the methyl groups which prevent the close grouping of the two reagent molecules around the metal in chelates of 2-methyl-8-hydroxyquinoline. The lower bond strength in chelates of 2-methyl-8-hydroxyquinoline is partially compensated by a relatively larger entropy of formation. This is attributed to decreased solvent chelate interaction caused by the shielding of the polar O, N, and metal atoms by the 2-methyl groups. The determination of chelate formation constants of 2-phenyl-8-hydroxyquinoline has been carried out to further extend our study of steric effects in metal chelates.

RÉSUMÉ

Les auteurs ont appliqué la technique de titrage de CALVIN-BJERRUM à la détermination des constantes de formation des complexes des 2- et 4-méthyl-8-hydroxyquinoléines avec Cu, Ni, Co, Zn et Mn. Les mesures ont été faites à diverses températures afin d'évaluer les valeurs de chélation $\triangle H$ et $\triangle S$. Les résultats obtenus ont été interprétés en fonction de l'empêchement stérique provenant du groupement 2-méthyl. Les chaleurs de formation des complexes de la 2-méthyl-8-hydroxyquinoléine sont toujours nettement plus positives que celles des com-

plexes de la 4-méthyl-8-hydroxyquinoléine. Cette grande différence dans les forces de liaison entre le métal et la molécule organique semble être due à l'empêchement stérique des groupes méthyl rendant très difficile la formation de chélate. La faible force de liaison dans les chélates de la 2-méthyl-8-hydroxyquinoléine est partiellement compensée par une relativement grande entropie. Cette dernière est attribuée à un affaiblissement de l'interaction entre le dissolvant et le complexe, les groupements méthyliques empêchant le réactif de réagir avec l'oxygène, l'azote et les atomes métalliques polarisés. Les auteurs ont déterminé également les constantes de formation des complexes de la 2-phényl-8-hydroxyquinoléine pour faire mieux comprendre l'importance des facteurs stériques dans le domaine des complexes.

ZUSAMMENFASSUNG

Die CALVIN-BJERRUMsche Titrationsmethode zur Bestimmung der Komplexbildungs-Konstanten ist auf die Cu(II)-, Ni(II)-, Co(II)-, Zn(II)- und Mn(II)-Komplexe des 2- und 4-Methyl-8-oxychinolins angewandt worden. Es wurden Messungen bei verschiedenen Temperaturen ausgeführt um die Wärmetönung und die Entropie der Komplexbildung zu bestimmen. Die Ergebnisse sind im Sinne sterischer Hinderung der 2-Methylgruppe gedeutet worden. In allen Fällen war die Wärmetönung der Komplexbildung der Komplexe des 2-Methyl-8-oxychinolins bemerkenswert positiver als die derselben Komplexe des 4-Methyl-8-oxychinolins. Dieser grosse Unterschied der Bindungsenergie der Metall-Komplexbindungen ist anscheinend auf die Methylgruppen, die eine dichte Gruppierung der zwei Reagenzmoleküle um das Metall in dem 2-Methyl-8-oxychinolinkomplex verhindern, zurückzuführen. Die kleinere Bindungsenergie der Komplexe des 2-Methyl-8-oxychinolins ist teilweise durch eine grössere Entropie kompensiert. Dies wird gedeutet als eine Verminderung der Wechselwirkung zwischen Komplex und Lösungsmittel durch Abschirmung der polaren O, N, und Metallatomen durch die Methylgruppen. Die Bildungskonstanten der Komplexe des 2-Phenyl-8-oxychinolins wurden bestimmt um unsere Forschung der sterischen Effekte in Metallkomplexen weiter ausendehnen.

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MERCUROUS SALTS AS NEW REDUCTIMETRIC REAGENTS FOR TITRATIONS IN ALKALINE MEDIUM

II. TITRATION OF CHROMIUM SALTS, ARSENITES, HYDROGEN PEROXIDE AND HYDRAZINE

by

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In the first part of this study[1] the optimum conditions were determined under which a mercurous salt quantitatively reduces the ferricyanide ion. The procedure can be applied to the determinations by back-titration of those substances which are oxidized by the ferricyanide ion in alkaline medium, adding excess ferricyanide and titrating the latter afterwards by the methods suggested.

We carried out a titration study of chromium salts, arsenious salts, hydrogen peroxide and hydrazine. In each case, the conditions of alkalinity and temperature under which the respective substance oxidizes quantitatively with the ferricyanide were determined. Afterwards, in every case, the excess of ferricyanide was titrated with a standard mercurous perchlorate solution at room temperature and adequate alkalinity.

I. TITRATION OF CHROMIUM SALTS

BOLLENBACH AND LUCHMANN[2] were the first to oxidize chromium salts in alkaline medium for analytical purposes by means of potassium ferricyanide. The chromate obtained was precipitated with $Ba(OH)_2$ and then they titrated the ferricyanide formed during the reaction by permanganimetry, in acid medium, according to HAHN's method. Later, HAHN[3] carried out a direct determination of the chromium salt with ferricyanide in a hot, strongly alkaline medium. However, he found that the reaction is slow and he suggests the addition of a small quantity of thallous salt to accelerate the reaction. DEL FRESNO AND VALDÉS[4] tried a successive titration of quadrivalent vanadium and chromium sulphate in alkaline medium with potassium ferricyanide, but did not obtain quantitative results.

Ferricyanide and trivalent chromium react in basic medium according to the equation:

$$3[Fe(CN)_6]^{-3} + Cr^{+3} + 8OH^- \longrightarrow 3[Fe(CN)_6]^{-4} + CrO_4^{-2} + 4H_2O$$

Hence it can be deduced that a strong concentration of NaOH is necessary to favour the displacement of the reaction towards the right, but an excessive concentration is not advisable, as it may decompose the ferricyanide according to the reaction:

$$[Fe(CN)_6]^{-3} + 3OH^- \longrightarrow Fe(OH)_3 + 6CN^-$$

and the CN^- ion formed, on being oxidized by unaltered ferricyanide, would cause further progress in the decomposition of the latter.

High temperature favours the oxidation of chromium by ferricyanide, but boiling temperature should not be reached as the ferricyanide would also decompose, as KASNER has shown[5].

In our determination we have shown that the above-mentioned oxidation of Cr^{+3} takes place almost instantaneously, even at room temperature, when a moderate excess of ferricyanide is added and the solution is made alkaline until it is approximately molar in NaOH. By titrating this excess ferricyanide with mercurous perchlorate, excellent results are obtained in determination of trivalent chromium.

EXPERIMENTAL PART

A $0.1000N$ solution of $K_2Cr_2O_7$ prepared from absolutely pure "Merck" salt, which had been dried at 130° C till constant weight, was used to prepare a standard solution containing Cr^{+3} by reducing with ethyl alcohol in an acid medium.

Procedure

Different volumes of $0.1000N$ dichromate solution were placed in a 300 ml beaker, from 10 to 20 ml HCl (1 : 1) were added and another 10 ml of pure absolute ethyl alcohol. This was heated until total reduction of the dichromate and expulsion of the excess alcohol and aldehyde produced by the oxidation.

Little by little $4M$ NaOH was added until the $Cr(OH)_3$ precipitate persisted, followed by an excess of 25 ml, whereupon the precipitate dissolved and formed chromite of an intense green colour;

$$Cr(OH)_3 + OH^- \longrightarrow CrO_2^- + 2H_2O$$

A moderate excess of standard $0.1N$ potassium ferricyanide was then added whereupon immediate oxidation of the chromite occurred, and the liquid turned completely yellow.

$$CrO_2^- + 3[Fe(CN)_6]^{-3} + 4OH^- \longrightarrow CrO_4^{-2} + 3[Fe(CN)_6]^{-4} + 2H_2O$$

40 ml of molar KI were then added and distilled water to 100 ml, and the added excess ferricyanide was titrated with mercurous perchlorate, the end-point being determined potentiometrically as indicated in the first part of the paper.

The results obtained are shown in Table I.

TABLE I

Solutions: 1.— 0.1*N* potassium ferricyanide, f = 0.982
2.— 0.1*N* mercurous perchlorate, f = 0.952
3.— 0.1000*N* potassium dichromate.

ml of $Cr_2O_7K_2$ 0.1000*N* added	ml of ferricyanide 0.1000*N* corrected added	ml of $(COl_4)_2Hg_2$ 0.1000*N* corrected used	ml of $Cr_2O_7K_2$ found	Difference %
5.00	19.64	14.66	4.98	−0.4
10.00	19.64	9.62	10.02	+0.2
15.00	19.64	4.67	14.97	−0.2
20.00	24.55	4.57	19.98	−0.1
25.00	34.36	9.43	24.93	−0.3
30.00	34.36	4.57	29.79	−0.7

As can be seen, the results obtained are satisfactory.

2. TITRATION OF ARSENITES

The oxidation of trivalent arsenic in alkaline medium by potassium ferricyanide for analytical purposes was first elaborated by PALMER[6]. He used a strongly alkaline medium of sodium hydroxide and employed five times more potassium ferricyanide than theoretically necessary; after oxidation he made the solution ammoniacal, precipitated the arsenite with magnesia mixture, filtered and titrated the ferricyanide by permanganimetry, according to HAHN.

DEL FRESNO AND VALDÉS[7] considerably simplified the process: in a very alkaline medium (25% of NaOH) and at 70° C they titrated arsenites with standard potassium ferricyanide directly. The end-point was determined potentiometrically.

WILLARD AND MANALO[8] treated the arsenite with excess ferricyanide in a basic medium of 3*N* sodium hydroxide and titrated the excess ferricyanide with vanadyl sulphate, in the absence of air. They used various derivatives of diphenylamine as end-point indicators.

In the present paper it is shown that, on oxidizing arsenite with excess ferricyanide and titrating the latter with mercurous perchlorate, excellent results are obtained in the determination of the arsenite ion.

EXPERIMENTAL PART

We have used a 0.1 sodium arsenite solution prepared with As_2O_3 by dissolving it in diluted NaOH. The solution is titrated iodometrically.

Procedure

In different precipitation beakers are placed different volumes of the arsenite solution, then excess ferricyanide is added, and finally, 25 ml of 4*M* NaOH.

The mixture is heated in a sand bath, not above 90° C, for 15-20 minutes; afterwards it is cooled and sufficient water added to give a final volume of 100 ml. 40 ml of molar KI are then added. The ferricyanide is titrated with mercurous perchlorate according to the usual procedure.

The results obtained are shown in Table II.

TABLE II

Solutions: 1.— 0.1N potassium ferricyanide, f = 0.982
2.— 0.1N mercurous perchlorate, f = 0.952
3.— sodium arsenite, 0.1N, f = 0.978.

ml of arsenite 0.1000N (corrected) added	ml of ferricyanide 0.1000N (corrected) added	ml of perchlorate 0.1000N (corrected) used	ml of arsenite 0.1000N found	Dif. %
4.89	9.82	4.95	4.87	—0.4
9.78	19.64	9.81	9.83	+0.5
14.67	19.64	4.95	14.69	+0.1
19.56	29.46	9.83	19.63	+0.3
24.45	29.46	5.03	24.43	—0.1
29.34	39.28	9.99	29.29	—0.2

3. TITRATION OF HYDROGEN PEROXIDE

In a sufficiently alkaline medium, hydrogen peroxide reacts with the ferricyanide ion, reducing and liberating elemental oxygen:

$$2[Fe(CN)_6]^{-3} + H_2O_2 + 2OH^- \longrightarrow 2[Fe(CN)_6]^{-4} + O_2 + 2H_2O$$

WILLARD AND MANALO[8] took advantage of this reaction to carry out direct titration of ferricyanide with hydrogen peroxide. We have observed that, by adding excess ferricyanide and titrating it with mercurous perchlorate, an excellent method for determining hydrogen peroxide is obtained.

EXPERIMENTAL PART

Procedure

In different beakers are placed volumes of 0.1N ferricyanide in quantities in excess of those required to oxidize the hydrogen peroxide, ***which is added afterwards***. 25 ml of 4M NaOH are then added and the test material containing the peroxide. This mixture is gently heated to 70-80° C and shaken until the evolution of gas ceases. Then it is cooled and sufficient water added to give a final volume of 100 ml, 40 ml of KI are added, titrating finally with standard mercurous perchlorate and the end-point is determined potentiometrically.

Table III shows the results obtained, expressed in normalities instead of as volumes oxygen.

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TABLE III

Solutions: 1.— 0.1*N* potassium ferricyanide, f = 0.982
2.— 0.1*N* mercurous perchlorate, f = 952
3.— hydrogen peroxide, 0.1*N*, f = 0.932.

ml of H_2O_2 1000*N* (corrected) added	ml of ferricyanide 0.1000*N* (corrected) added	ml of perchlorate 0.1000*N* (corrected) used	ml of H_2O_2 0.1000*N* found	Dif. %
4.66	9.82	5.19	4.63	—0.6
9.32	19.64	10.35	9.29	—0.3
13.98	19.64	5.62	14.02	+0.3
18.60	29.46	10.76	18.70	+0.5
23.30	29.46	6.19	23.27	—0.1
27.96	39.28	11.43	27.85	—0.4

4. TITRATION OF HYDRAZINE

In basic medium, hydrazine is oxidized by ferricyanide liberating nitrogen:

$$NH_2.NH_2 + 4[Fe(CN)_6]^{-3} + 4OH^- \longrightarrow N_2 + 4[Fe(CN)_6]^{-4} + 4H_2O$$

The literature gives two principal methods, based on this reaction, for the titration of hydrazine or its salts.

The first, due to Dernbach and Mehlig[9], is based on the oxidation of the test material, made alkaline with NaOH, with excess ferricyanide, followed by acidification and determination of the ferricyanide formed with ceric sulphate.

The second, due to Willard and Manalo[8], also makes use of excess ferricyanide for oxidation in basic medium; the ferricyanide not reduced is titrated with vanadyl sulphate, in the absence of air.

In the method proposed, oxidation is carried out with standard excess ferricyanide in a moderately diluted basic medium (1*M* in NaOH), whereby oxidation of the hydrazine by atmospheric oxygen is avoided. This can occur at a high pH, as mentioned by various authors[10]. In this way, the oxidation of the base is slower, though it can be accelerated by shaking or gentle heating at 50-60° C. The non-reduced excess ferricyanide is titrated with mercurous perchlorate, or nitrate without having to exclude air.

EXPERIMENTAL PART

An 0.1*N* hydrazine hydrate solution was prepared from a Schering solution with 50% concentration and d = 1.02.

The solution was titrated iodometrically by the procedure of Bray and Cuy[11].

Procedure

To different volumes of the hydrazine solution was added at least twice as much 0.1*N* ferricyanide and then the same quantity of 2*N* NaOH. This is shaken and if necessary gently heated to 60° C.

When the evolution of nitrogen has ceased, the solution is left to cool, 40 ml of 1*M* KI are added and sufficient water to obtain a final volume of 100 ml. Then it is back-titrated with 0.1*N* $Hg_2(ClO_4)_2$ by the usual procedure.

The results obtained are given in Table IV.

TABLE IV

Solutions: 1.— 0.1*N* potassium ferricyanide, f = 0.982
2.— 0.1*N* mercurous perchlorate, f = 0.952
3.— hydrazine hydrate 0.1*N*, f = 0.950.

ml of hydrazine 0.1000*N* (corrected) added	ml of ferricyanide 0.1000*N* (corrected) added	ml of $(ClO_4)_2Hg_2$ 0.1000*N* (corrected) used	ml of hydrazine 0.1000*N* found	Dif. %
4.75	19.64	14.92	4.72	—0.6
9.50	19.64	10.64	9.48	—0.2
14.25	29.46	15.17	14.29	+0.3
19.00	29.46	10.38	19.80	+0.4
33.75	39 23	15.47	23.81	+0.2
28.50	39.28	10.88	28.40	—0.4

SUMMARY

In this second note we have studied the titration of chromium salts, arsenites, hydrogen peroxide and hydrazine. These substances can be oxidized quantitatively in alkaline medium by a moderate excess of ferricyanide ion. This excess is afterwards determined by a standard solution of mercurous salt according to the method suggested in the first part of the paper[1].

In each case the most suitable conditions of alkalinity and temperature were established for carrying out the determination.

RÉSUMÉ

Dans ce deuxième article, les auteurs ont étudié la titration des sels de chrome(III), des arsénites, du peroxyde d'hydrogène et de l'hydrazine. Ces composés peuvent être oxydés quantitativement en solution alcaline, par l'anion ferricyanhydrique, en léger excès. Cet excès est ensuite titré par une solution étalon et un sel de mercure (I) suivant la méthode proposée dans la première partie de ce travail[1]. Dans chaque cas, les meilleures conditions d'alcalinité et de température, pour effectuer des dosages, ont été établies.

ZUSAMMENFASSUNG

In dieser zweiten Arbeit haben die Autoren die Titration der Chrom(III)salze, der Arsenite, des Wasserstoffperoxydes und des Hydrazins untersucht. Diese Verbindungen können in alkalischer Lösung quantitativ oxydiert werden durch das Ferricyanid-Anion in leichtem Überschuss. Dieser Überschuss wird dann mit einer Vergleichslösung und einem Quecksilber(I)salz titriert nach der Methode, die im ersten Teil dieser Arbeit vorgeschlagen wurde[1]. Für jeden Fall wurden die besten Bedingungen betr. Alkalinität und Temperatur für die Technik der Analyse festgelegt.

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RESUMEN

En esta segunda nota estudiamos la valoración de sales crómicas, arsenitos, peróxidos de hidrógeno e hidracina, substancias que son oxidades cuantitativamente, en medio alcalino, por el ión ferricianuro en moderado exceso. Este exceso es posteriormente determinado por una solución valorada de sal mercuriosa de acuerdo con el método propuesto en la primera nota de este trabajo[1].

En cada caso se establecen las condiciones de alcalinidad y temperatura màs adecuados para efectuar la determinación.

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LA DÉTERMINATION RAPIDE DU CALCIUM ET DU MAGNÉSIUM DANS L'EAU DE MER

par

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L'eau de mer est une solution beaucoup plus complexe que ne le laissent supposer les analyses. Déjà en 1865, FORSCHAMMER[1] signalait 32 éléments déterminés par l'analyse chimique. La biologie maritime a basé son explication de l'existence de certains êtres vivants, ainsi que de l'absence d'autres, en fonction de la composition chimique de l'eau[2].

Suivant VERNADSKY[3] qui a donné des concentrations moyennes de 27 éléments existants dans 100 g d'eau de mer, nous notons dans l'ordre décroissant des concentrations, que le magnésium occupe la seconde place parmi les cations et le calcium la quatrième. Cet auteur indique 0.14 g de Mg^{+2} et 0.05 g de Ca^{+2} par 100 g d'eau. Or, à part les métaux alcalins (Na et K), le dosage du calcium et du magnésium est d'une grande importance pour la biologie maritime.

Malheureusement, la détermination de ces deux éléments est longue et comme nous l'avons dit dans un travail précédent[4], susceptible d'être faussée par la richesse en chlorures de l'échantillon.

Les valeurs indiquées par VERNADSKY peuvent être considérées comme indication de l'ordre de grandeur, vu que la composition chimique de l'eau de mer prélevée en un lieu et à un moment donné, est la résultante en ce point et en ce temps, de toutes les activités diverses qu'elle subit. Ainsi le pH, la salinité, la concentration des ions importants Ca^{+2} et Mg^{+2} sont responsables de l'existence de certaines espèces, de leur migration ou de leur disparition.

Alors que la concentration des ions H^+ et la salinité peuvent être déterminées rapidement, la teneur en calcium et en magnésium prend un temps considérable si l'on a recours aux méthodes usuelles de la gravimétrie. Le biologiste doit avoir des résultats rapides, une très grande rigueur n'étant pas absolument nécessaire. Une des méthodes les plus rapides que nous avons expérimentée est celle de la titration directe de l'eau de mer à l'aide du complexon III* (sel disodique de l'acide éthlylène-diaminotétracétique) en utilisant deux indicateurs*. Les autres ions contenus dans l'eau de mer n'interfèrent pas. Grâce à la faible teneur en fer

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* La maison B. Siegfried (Zofingue, Suisse) a bien voulu mettre à notre disposition des échantillons, ainsi que les indicateurs nécessaires pour nos essais.

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(0.0001 à 0.0002 g par 100 g d'eau de mer) et de faibles traces d'aluminium, l'erreur commise par le dosage complexométrique est négligeable.

Nous avons obtenu des résultats très satisfaisants avec différents échantillons d'eau de mer puisés à l'embouchure du Tage, en différents endroits de la côte portugaise et en haute mer. Les valeurs obtenues par la gravimétrie concordent de très près avec celles de la volumétrie complexométrique; cette dernière permet d'obtenir des résultats en Ca^{+2} et Mg^{+2}, dans l'espace d'une heure, alors que par les méthodes classiques de la gravimétrie, nous avons dû attendre souvent plus de 48 heures et prendre des précautions spéciales.

Signalons un autre avantage de la méthode complexométrique sur celles de la gravimétrie: les déterminations peuvent être faites „in loco" ou pendant une croisière et conviennent pour les expéditions océanographiques où l'emploi de la balance de précision et les opérations de précipitation, filtration en calcination ne sont pas toujours faciles à réaliser.

Nous avons basé notre technique sur les travaux de SCHWARZENBACH et ses collaborateurs[5]. Lorsqu'on titre une solution contenant du calcium par une liqueur titrée de complexon III, en présence d'un indicateur spécifique, la murexide, on observe un virage très net quand tous les ions Ca^{+2} sont complexés. Ainsi, on peut calculer la teneur en calcium, connaissant le titre de la solution de complexon.

Le magnésium n'a pas d'indicateur spécifique, le noir d'ériochrome T, réagit aussi en présence des ions Ca^{+2}. Mais ce dernier indicateur permet de doser la somme des ions Ca^{+2} et Mg^{+2}, par différence on peut calculer la quantité de Mg^{+2} présent.

TECHNIQUE OPÉRATOIRE

100 ml d'eau de mer sont introduits dans un bécher pour la détermination du calcium. Une solution d'hydroxyde de sodium est ajoutée goutte à goutte jusqu'à ce que le pH de la solution soit légèrement supérieur à 12. On ajoute assez de solution de murexide pour donner une forte coloration rouge à la solution saline. On titre à l'aide d'une micro-burette et en se servant d'une solution $0.1M$ de complexon III jusqu'à ce que l'indicateur vire au bleu violet. On calcule la quantité de Ca^{+2} présent, sachant que 1 ml du réactif complexant correspond à 4.008 mg de calcium.

On dissout 37.21 g du sel disodique de l'acide diaminotétracétique dans un peu d'eau bidistillée et l'on complète le volume à 1000 ml.

Solution aqueuse saturée de murexide (purpurate d'ammonium). On agite 0.1 g d'indicateur avec 100 ml d'eau et l'on filtre. La solution d'indicateur ne se conserve que quelques jours; on recommande de préparer de petites quantités fraîches pour obtenir des virages nets.

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DOSAGE DU MAGNÉSIUM

100 ml d'eau de mer sont introduits dans un bécher. On ajoute environ 1 ml d'indicateur (noir ériochrome T) et 10 ml de solution tampon ($NH_4Cl + NH_4OH$), on chauffe entre 40 et 50° C. A ce moment-là on titre la solution avec une liqueur $0.1M$ de complexon III (la même qui a servi pour le dosage de calcium), jusqu'à ce que la solution vire du rouge vineux au bleu. Il est indispensable que la température ne soit pas inférieure à 40° C pour que le virage soit net. La quantité de Mg^{+2} contenue dans l'échantillon s'obtient par différence. Soit N le nombre de ml du réactif complexant nécessaire pour complexer le calcium et N' le nombre de ml nécessaire pour la somme $Ca^{+2} + Mg^{+2}$. Sachant que 1 ml correspond à 2.432 mg de Mg^{+2}, la teneur en magnésium en mg/100 ml sera donnée par $(N' - N) \times 2.432$.

SOLUTIONS NÉCESSAIRES

0.4 g de noir ériochrome T dans 100 ml d'alcool absolu.

On introduit dans un ballon jaugé de 1000 ml, 54 g de chlorure d'ammonium et 350 ml d'ammoniaque à 25% et l'on complète avec de l'eau jusqu'au trait de jauge.

CONCLUSIONS

Comme nous l'avons dit au début, la méthode complexométrique est la plus rapide et la plus pratique pour l'étude du calcium et du magnésium dans l'eau de mer. Vu la simplicité de la technique, les déterminations peuvent être effectuées sur place et même en pleine mer. Les résultats sont très satisfaisants et peuvent être obtenus au bout d'une heure environ.

RÉSUMÉ

Une méthode rapide est décrite pour le dosage du calcium et du magnésium dans l'eau de mer. Les méthodes classiques de la gravimétrie sont très longues et susceptibles d'erreurs lorsqu'elles sont appliquées à l'eau de mer. Ces deux éléments sont dosés par titrage complexométrique, en employant le complexon III (sel disodique de l'acide éthylènediaminotétracétique) comme réactif et deux indicateurs (la murexide et le noir ériochrome T) pour la détermination du calcium et pour celle de la somme des ions Ca^{+2} et Mg^{+2}. La quantité de magnésium est obtenue par différence. Alors que les méthodes classiques de la gravimétrie exigent au moins 24 heures, les deux déterminations peuvent être effectuées dans l'espace d'une heure et avec une précision satisfaisante.

SUMMARY

A rapid method is described for the determination of calcium and magnesium in sea water. The classical gravimetric methods are very lengthy and are susceptible to errors if used for sea-water. The two alkaline earths are determined by complexometric titration using complexon III (disodium ethylenediaminetetra-acetate) as reagent and two indicators (murexide and ériochrome black T) for the determination of calcium and for the sum of Ca^{+2} and Mg^{+2} ions. The quantity of magnesium is obtained by difference. While the classical gravimetric methods take at least 24 hours, these two determinations can be effected in 1 hour, giving satisfactory accuracy.

Bibliographie p. 224.

ZUSAMMENFASSUNG

Es wurde eine rasche Methode zur Bestimmung von Calcium und Magnesium im Meerwasser beschrieben. Die klassischen gravimetrischen Methoden sind sehr langwierig und ergeben unrichtige Werte, wenn sie für Meerwasser angewendet werden. Die beiden Alkalierden werden durch komplexometrische Titration unter Verwendung von Komplexon III (dem Dinatriumsalz der Äthylendiaminotetraessigsäure) als Reagenz und mit Murexid und Eriochromschwarz T als Indikator zur Bestimmung des Calciums und der Summe von Calcium und Magnesium bestimmt. Die Menge des Magnesiums ergibt sich aus der Differenz. Während die klassischen Methoden mindestens 24 Stunden erfordern, können die beiden Bestimmungen in einem Zeitraum von 1 Stunde und mit befriedigender Genauigkeit ausgeführt werden.

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ONE STEP DIGESTION PROCEDURE FOR THE ESTIMATION OF TOTAL PHOSPHORUS AND NITROGEN IN MOULD TISSUE

by

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Recently WHITE AND LONG[1], and GRUNBAUM, SCHAFFER AND KIRK[2] pointed out that the estimations of total nitrogen and phosphorus can be carried out on the same digest, when the digestion is effected in a sealed tube in the absence of added metal catalyst. In experiments designed to study the relation between phosphate and nitrogen metabolism in moulds the present authors had the necessity of digesting mycelial material with sulphuric acid and hydrogen peroxide in open tubes prior to the estimation of the total phosphate by the colorimetric method of SUMNER[3]. If these digests obtained with acid and peroxide could be utilized for the assay of total nitrogen also, a separate digestion of the mould tissue with sulphuric acid and metal catalyst would not be necessary for nitrogen estimation. As early as 1924 KOCH AND MCMEEKIN[4] reported that the addition of hydrogen peroxide to a solution of organic matter in concentrated sulphuric acid caused a very rapid oxidation with complete retention of nitrogen as ammonia and recommended the method for the determination of total nitrogen in biological material. MILLER AND MILLER[5] made a detailed study of the method of KOCH AND MCMEEKIN[4] and confirmed its applicability to biological samples. However, KIRK[6], in his review on the Kjeldahl method, expressed doubts about the general applicability of the digestion procedure with oxidizing agents, and stated that the influence of hydrogen peroxide on Kjeldahl digestion should be studied further. The present authors have, therefore, undertaken a comparative study of the digestion with sulphuric acid and hydrogen peroxide on the one hand, and with the acid and metal catalyst on the other, with special reference to mould tissue.

EXPERIMENTAL

The mould preparations used in the analysis consisted of either dried or acetonized mycelia. Fairly large samples *viz.* 250-500 mg, were taken so as to minimize any sampling errors. These were weighed into 50 ml Kjeldahl flasks and washed down with 4-6 ml of B.D.H. AnalaR sulphuric acid. Some of the flasks were used for digestion in the conventional manner with metal catalyst made up of selenium, copper sulphate and potassium sulphate[6]. The rest of the flasks were used for digestion with added hydrogen peroxide. The flasks were heated gently over gas burners until the solid material dissolved. The solutions were then heated strongly and when they started fuming the tubes were cooled for 15-30 seconds and 2-4 drops of Merck's 'Superoxol' were added along the sides. The heating was continued, and every 15 minutes 2-4 drops more of peroxide were added until the solution became completely colourless. Not more than 20 drops of hydrogen peroxide were needed. The heating was continued for 30 minutes more. The digests were cooled, diluted with water and boiled for about 3 minutes. This

TABLE I

ESTIMATION OF TOTAL NITROGEN IN MOULD TISSUE

		Digested with $H_2SO_4 + H_2O_2$	Digested with H_2SO_4 + metal catalyst
		µg/mg dry weight	
Aspergillus niger, dried to constant weight	12 days in Currie's medium	39.7	39.8
Aspergillus oryzae, dried to constant weight	2 days in Czapek-Dox medium with yeast extract	63.4	64.9
	3 days in the same medium	59.4	59.2
Penicillium chrysogenum, acetonized.	6 days in Czapek-Dox medium	56.7	55.9
	4 days in Czapek-Dox medium, with yeast extract	74.7	73.0
Neurospora sitophila, dried to constant weight	3 days in Fries' medium	98.9	97.8
	5 days in the same medium	89.1	90.6
Rhizopus, dried to constant weight	7 days in Czapek-Dox medium, with yeast extract	61.1	59.8
	9 days in the same medium	56.7	56.6

was necessary in order to decompose any phosphoric anhydrides before estimation of orthophosphate. The digestion was complete within about 6 hours when hydrogen peroxide was used, but took at least 2-4 hours more when the metal catalyst was used. The digests were made up to 50 ml and aliquots containing 0.3-0.5 mg nitrogen removed for estimation by distillation of the ammonia into excess acid. Two sets of blank digests of sulphuric acid were run simultaneously, one with the metal catalyst, and the other heated with as many drops of hydrogen peroxide as were used in the experiments. Data obtained in typical experiments are recorded in Table I. The results were reproducible within the range ± 1.5%.

It is apparent from the data given in Table I that identical values for total nitrogen are obtained, whether the samples are digested with sulphuric acid and hydrogen peroxide, or with the acid and metal catalyst. In other experiments the mould tissue was digested with sulphuric acid and hydrogen peroxide and made up to volume. Nitrogen estimations were carried out on aliquots of this solution and also on other aliquots which had been further digested with added sulphuric acid and selenium-copper sulphate-potassium sulphate mixture. Very similar titre values were obtained, showing that the digestion was complete with sulphuric acid and hydrogen peroxide.

Application to other biological material

The data reported in Table II show that the digestion procedure with sulphuric acid and hydrogen peroxide can be applied also to animal tissue, vegetable matter and bacteria. In every case it was observed that the digestion with the acid and peroxide took a shorter time than with the acid and metal catalyst.

TABLE II

ESTIMATION OF TOTAL NITROGEN IN BIOLOGICAL MATERIAL

	Digested with $H_2SO_4 + H_2O_2$	Digested with H_2SO_4 + metal catalyst
	μg/mg dry weight	
Acetonized liver (buffalo)	133.7	132.3
Ground-nut cake	75.0	74.8
Acetonized *B. cadaveris*	128.5	124.0

References p. 228.

ACKNOWLEDGEMENTS

The authors' thanks are due to Dr. M. DAMODARAN for his interest in the investigation. One of us (S.P.D.) is grateful to the Council of Scientific and Industrial Research, and to the Director, National Chemical Laboratory, for permission to work in this Laboratory.

SUMMARY

The estimation of total phosphorus and nitrogen in mould tissue and other biological material can be carried out in a common digest prepared with sulphuric acid and hydrogen peroxide.

RÉSUMÉ

Les auteurs recommandent l'attaque à l'acide sulfurique - eau oxygénée pour le dosage simultané du phosphore et de l'azote total dans les moisissures et dans d'autres substances biologiques.

ZUSAMMENFASSUNG

Die Autoren empfehlen eine Behandlung mit Schwefelsäure und Wasserstoffperoxyd für die gleichzeitige Bestimmung von Phosphor und von Stickstoff in Schimmelpilzen und andern biologischen Substanzen.

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NEUES ANEMOMETER MIT BELIEBIG EINSTELLBAREM MESSBEREICH FÜR KLEINE STROMSTÄRKEN

von

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Im Laboratorium sind recht häufig Stromstärkemessungen von Gasen auszuführen. Bei Stabilitätsuntersuchungen an Fetten waren Sauerstoff und Luft, welche in Mengen bis zu 6 ml/sec durch erhitztes Fett geleitet werden, exakt zu messen.

Meistens wird bei den Strömungsmessern für kleine Stromstärken der Druckabfall längs einer Kapillare bestimmt.

Für laminare Strömung ist nach dem Gesetz von HAGEN UND POISEUILLE das in der Zeiteinheit aus einem Rohr vom Radius r und der Länge l unter der Druckdifferenz $p_1 - p_2$ ausströmende Gasvolumen V durch die Gleichung

$$V = \frac{l}{\eta} \frac{\pi r^4}{8l} (p_1 - p_2)$$

gegeben. Hierbei is η Koeffizient der innern Reibung. Dieser hängt von der Natur des Gases und vond der Temperatur ab.

Der Proportionalitätsfaktor zwischen Stromstärke und gemessenem Druckabfall wird durch Eichung festgelegt.

Die Eichkurven werden für jedes Gas in Abhängigkeit von der Temperatur aufgenommen.

Will man mit einem solchen Instrument bei optimaler Empfindlichkeit messen, muss der Messbereich variabel sein. Der Messbereich ist einerseits gegeben durch die Abmessung von Kapillare und Manometer, anderseits durch das spezifische Gewicht der Manometerflüssigkeit.

Bei starrer Konstruktion des Anemometers kann dieser nur durch geeignete Wahl der Manometerflüssigkeit verändert werden. Es ist nicht einfach, eine Skala verwendbarer Flüssigkeiten aufzustellen, da die Auswahl ausser vom spezifische Gewicht noch von Viskosität, Benetzungsvermögen, Siedepunkt und dem zu messenden Gas abhängt. Zudem sind die Instrumente nicht zum bequemen Auswechseln der Manometerflüssigkeit eingerichtet.

Häufig wird die Kapillare auswechselbar angeordnet. F. ROHNER[1] gibt eine kritische Übersicht dieser Konstruktionen. Zusammenfassend kann ihr entnommen werden, dass bei kompliziertem Aufbau die Messbereiche mühelos umschaltbar sind, die Messgenauigkeit anscheinend aber zu wünschen übrig lässt.

Auch das Anemometer, wie es ROHNER vorschlägt, zeigt Mängel. Die Eichkurve ist nicht linear und die Umstellung des Instrumentes auf verschiedene Messbereiche kompliziert.

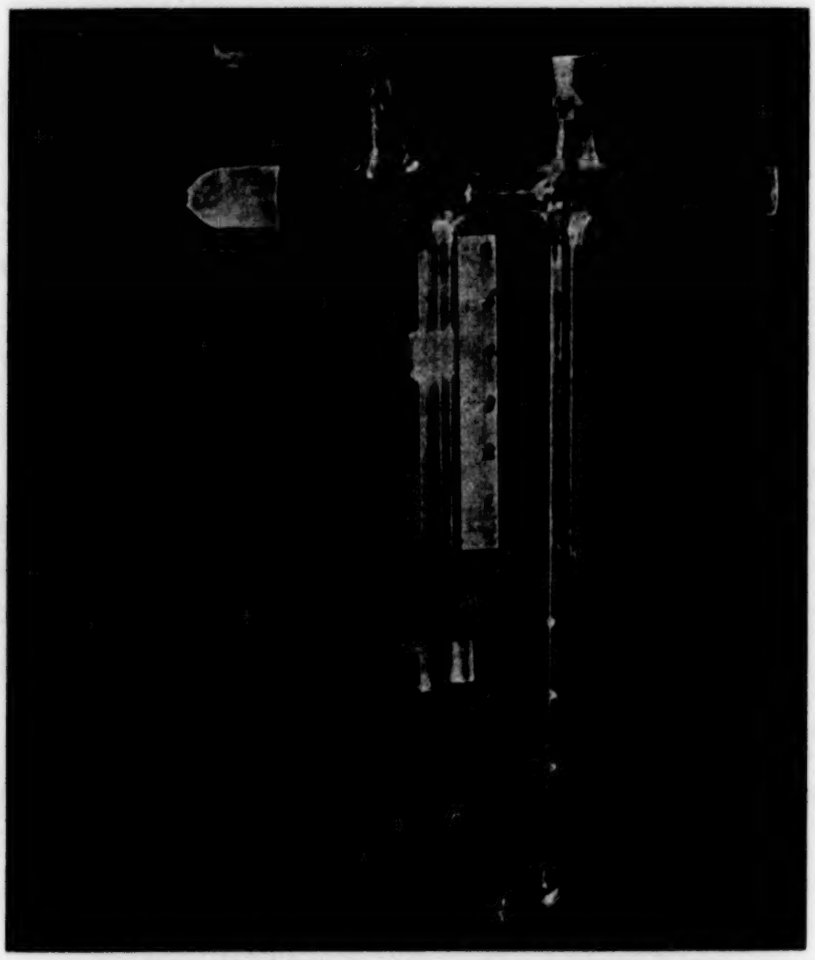

Abb. 1. Anemometer $^1/_2$ nat. Grösse

Abb. 1 zeigt das neue Anemometer. Es ist ganz aus Glas angefertigt, mit Ausnahme der im toten Raum angebrachten Gummidichtung. Diese lässt sich nötigenfalls durch eine resistente Membran schützen.

Aus der Abb. 2 ist das Prinzip des Strömungsmessers ersichtlich. Das Instrument besitzt eine Kapillare mit kreisringförmigem Querschnitt.

Für die Durchflussmenge aus einem Hohlzylinder lässt sich eine ähnliche Beziehung wie das HAGEN — POISEUILLESCHE Gesetz herleiten. Die Stromstärke ist auch hier dem Druckabfall direkt proportional. Der Kapillarwiderstand und damit der Messbereich lassen sich durch einen in der Kapillare verschiebbaren Glaskonus kontinuierlich ändern. Durch Markieren der Position der Konusspitze auf dem Instrument werden die Eichstellungen festgehalten.

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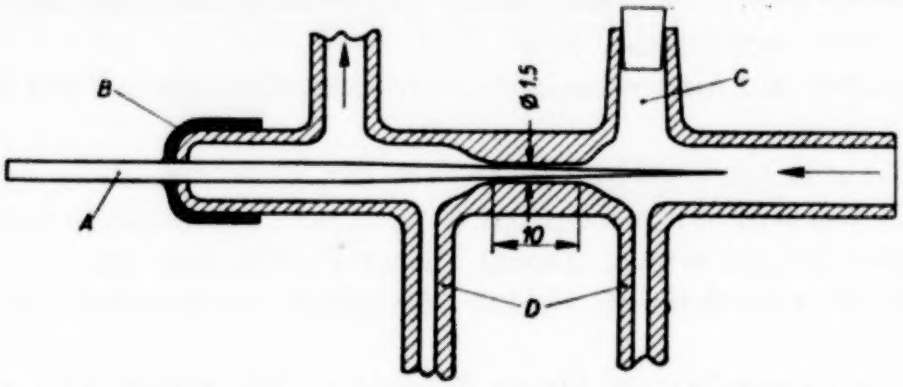

Abb. 2. A. Glaskonus; B. Gummidichtung; C. Ansatz zum Füllen des Manometers; D. Manometer.

Das Anemometer zeigt bis zu etwa 6 ml Durchfluss/sec lineare Abhängigkeit zwischen Druckabfall (Manometerstand) und Stromstärke. Zur Eichung genügt deshalb pro Empfindlichkeitsstufe eine Messung.

Mit Rücksicht auf einen bequemen Einbau wurde auf die übliche Bauart als Standinstrument verzichtet und die Skala direkt am Manometer befestigt. Sie ist aus durchsichtigem Kunststoff gefertigt (biegen im Dampfstrahl), lässt sich in der Längsrichtung verschieben und um den Manometerschenkel drehen, was ein müheloses Ablesen gestattet.

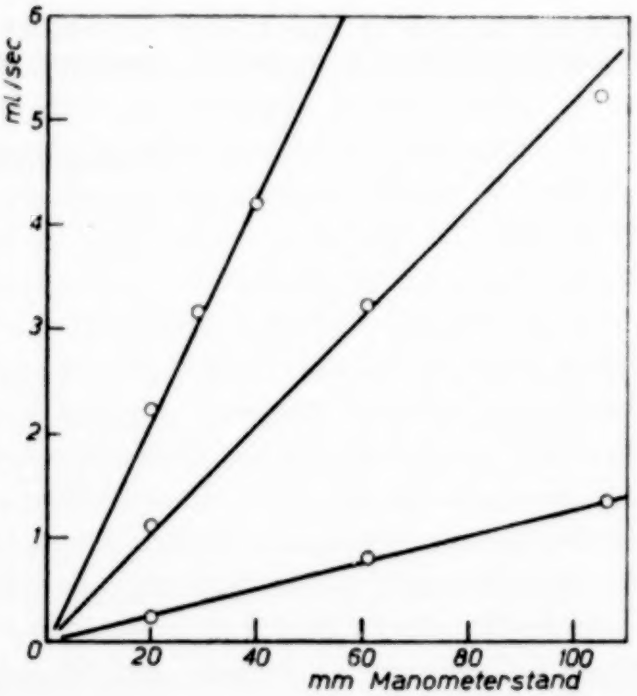

Abb. 3. Eichkurven für Luft bei 20°. Drei verschiedene Empfindlichkeiten.

Als Manometerflüssigkeit dient angefärbtes Wasser, welches ein Netzmittel enthält.

Der Netzmittelzusatz setzt die Oberflächenspannung soweit herab, dass, auch bei nicht überall gleichem Durchmesser der Manometerröhre, die Kapillarität die Messung nicht beeinflusst.

Zum Nachfüllen und Auswechseln der Manometerflüssigkeit dient der Ansatz *C*.

In der Literatur sind zahlreiche Geräte zur Durchflussmessung von Gasen vorgeschlagen worden. Wir verzichten darauf, eine Literaturübersicht zu geben, da dies zu weit führen würde. Zweck dieser Publikation ist es, auf eine einfach herstellbare und dennoch exakte Messapparatur hinzuweisen.

An dieser Stelle möchte ich Herrn POTTERAT, Ing. Chem., für die wertvollen Ratschläge bei der praktischen Ausführung des Instrumentes danken.

ZUSAMMENFASSUNG

Es wird ein einfaches, genaues Anemometer mit beliebig einstellbarem Messbereich beschrieben. Ein Manometer misst den Druckabfall längs einer hohlzylinderförmigen Kapillare mit veränderlichem Querschnitt.

SUMMARY

Description of a new and simple anemometer with adjustable sensibility by varying the diameter of the capillary tube by means of a conical glass rod.

RÉSUMÉ

On décrit un anémomètre simple et exact avec sensibilité ajustable à volonté en faisant varier le diamètre du capillaire au moyen d'une baguette de verre conique.

Eingegangen den 9. April 1954

DETERMINATION OF BORON IN TITANIUM ALLOYS BY MEANS OF ION EXCHANGE

by

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INTRODUCTION

Recently a method was proposed by this laboratory[2] for the determination of boron in titanium alloys. In this method the boron is distilled as methyl borate and the boron determined colorimetrically with dianthramide. The method is accurate but is rather long. Also, it is not applicable to the determination of more than 0.1 per cent. boron. An investigation was undertaken to develop a rapid procedure for the determination of moderate amounts of boron that would use ion exchange. A method was finally developed which was applicable to titanium alloys containing 0.025 to 1 per cent. boron. In this method one or two grams of the sample are dissolved in hydrochloric acid, and the titanium and boron are oxidized with nitric acid. The solution is passed through a cation exchange column to remove the bulk of the titanium. A calcium carbonate separation is made to remove the residual titanium and adjust the acidity. The boron is then titrated with standard alkali after the addition of mannitol.

MARTIN AND HAYES[8] have described a procedure for the determination of boron after an ion exchange separation. Their procedure is not applicable to titanium alloys, because only about 98 to 99 per cent. of the titanium contained in a 1- or 2-gram sample can be removed by a cation exchanger. This is probably due to the fact that a rather high acidity is needed to hold titanium in solution, and the effectiveness of a cation exchanger decreases with increasing acidity. It was found that by using a calcium carbonate separation[7,11,12] the residual titanium left in solution could be readily removed. This calcium carbonate separation also serves to remove such elements as tungsten, silicon and phosphorus, which are not removed by the cation exchanger and can interfere with the titration. The application of the calcium carbonate separation directly to titanium alloys without a prior ion exchange separation of the titanium is valueless. The data of WHERRY AND CHAPIN[12] show that boron is occluded chemically by the calcium carbonate precipitate when large amounts of aluminum and iron are present.

References p. 238.

It was found in this laboratory that titanium causes much more occlusion of the boron than does aluminum or iron.

Various investigators[7 11,12] have used asbestos as a filtering aid in the calcium carbonate separation. It was found in this laboratory that the use of asbestos led to high blanks, so its use is not recommended. Another cause of high blanks observed by the authors is the common practice of preparing carbonate-free sodium hydroxide for the titration by allowing a 50 per cent. solution of the alkali to stand in a pyrex test tube (high boron glass) in precipitating out the carbonate. The use of boron-free glass to store the 50 cent. sodium hydroxide is recommended. The blanks obtained by the authors were very low (0.10 ml).

After filtering off the calcium carbonate precipitate, the pH of the solution is such that boric acid is the only free acid present. Boric acid is a very weak acid and cannot be titrated as such. However, by adding a polyalcohol, such as mannitol[1,3,4,7,10,11,12], glycerol[4 10] or invert sugar[4,8], the boric acid is transformed into a strong complex acid that can be readily titrated with standard alkali. Mannitol is the preferred polyalcohol for the purpose, since it is the most effective and does not require a prior adjustment of its pH.

Before titrating with the standard alkali, the solution should be cooled to about 10° to 15° C. It was found that if a slightly warm solution were titrated, the end-point was not sharp. This is due to the fact that the stability of the complex acid falls off rapidly as the temperature increases[5].

It is important that no ammonium salts be present during the titration[6,10]. This precludes the use of an ammoniacal separation of the residual titanium from the boron. Also, the interference from ammonium ion had to be borne in mind in choosing salts for a study of interferences. At the acidity used, ammonium ion is very incompletely removed from solution by a cation exchanger.

For the preparation of standard boron solution needed in the method, it is necessary to use boron oxide prepared by fusing boric acid. While boric itself is satisfactory for the preparation of a standard boron solution used for small amounts of boron, it should not be used for the preparation of a standard boron solution used for larger amounts of boron, since reagent grade boric acid may contain as little as 99.5. per cent boric acid[9].

The most effective ion exchange resin for the removal of titanium was found to be Dowex 50. This resin should receive a prior treatment with hydrochloric acid (1 to 2) in order to remove the very fine particles. The resin can be regenerated by passing hydrochloric acid (1 to 2) through the column. This regeneration treatment is not effective if the resin is treated with hydrochloric acid in a beaker. After about five determinations, the resin should be discarded, since undissolvable titanium accumulates in it.

APPARATUS AND REAGENTS

Dowex 50 ion exchange resin.

"Chromatographic tube" with detachable fritted glass base (Scientific Glassware Apparatus Co., Bloomfield, N. J.). The tube is 3 cm in diameter and 22 cm in height.

Glass wool.

Standard sodium hydroxide solution (approximately 0.05*N*). Dissolve 100 gram of cp sodium hydroxide pellets in 100 ml of water contained in a boron-free 300 ml Erlenmeyer flask. Cover with a rubber stopper and allow to stand for several days so that the carbonate settles out. Decant 5 ml of the solution into a 2.5-liter acid stock bottle containing about 2 liters of freshly boiled and cooled water. Shake and cover with a rubber stopper. Standardize by adding 20 ml of standard boron solution to 1-gram portions of titanium metal, and carrying the samples through the procedure.

Standard boron solution (1 ml = 0.5 mg boron). Fuse about 8 grams of boric acid by heating in a platinum dish over the strong heat of a Meker burner. Remove the flame and allow the melt to solidify. While still warm, transfer the melt to a weighing bottle and place in a desiccator. Dissolve 1.6092 grams of the boron oxide (B_2O_3) in water and dilute to 1 liter in a volumetric flask.

Nitric acid (1 to 1). Mix 1000 ml of nitric acid and 1000 ml of water.

Hydrochloric acid (1 to 1). Mix 1000 ml of hydrochloric acid and 1000 ml of water.

Hydrochloric acid (1 to 2). Mix 800 ml of hydrochloric acid and 1600 ml of water.

Hydrochloric acid (2 to 100). Mix 20 ml of hydrochloric acid and 1000 ml of water.

Phenolphthalein indicator solution. Dissolve 1 gram of reagent in 100 ml of neutral ethyl alcohol, and dilute to 200 ml with water.

Calcium carbonate, cp.

Mannitol, reagent grade.

PROCEDURE

Weigh the sample into a 300 ml boron-free Erlenmeyer flask with a ground glass joint. For samples containing 0.025 to 0.5 per cent. boron, use a 2-gram sample. For samples containing 0.5 to 1 per cent. boron, use a 1-gram sample. Dissolve the sample with 20 ml of hydrochloric acid (1 to 1) by heating under reflux. After solution is complete, wash down the condenser with a little water and disconnect the flask. To the hot solution add nitric acid (1 to 1) dropwise until the color of the blue titanous ion disappears, and then add a drop or two excess nitric acid (1 to 1). Dilute to about 150 ml with water.

Place about 80 grams of Dowex 50 ion exchange resin into a 600 ml beaker.

Add about 150 ml of hydrochloric acid (1 to 2) and stir. Allow to settle about a minute and pour off the solution. Repeat this treatment with a second portion of hydrochloric acid. Transfer the resin to an ion exchange tube, the bottom of which has been packed to a depth of one inch with a layer of glass wool. Wash the resin with hydrochloric acid (1 to 2) and then a few times with water.

Pour the solution of the sample through the column and wash with hydrochloric acid (2 to 100). Collect the effluent in a 500 ml Erlenmeyer flask which has a ground glass joint. To the effluent add calcium carbonate in small portions until the acid is neutralized and then add several grams excess calcium carbonate. Heat to boiling under reflux and boil for 30 minutes or more. Filter immediately through a fine filter paper (Whatman No. 42) and wash with boiling water. Cool the filtrate in an ice bath to about 10° to 15° C. Add about 2 grams of mannitol and 10 drops of phenolphthalein indicator solution and titrate to a pink color with standard sodium hydroxide solution. Add 2 more grams of mannitol, and if the color disappears, add more sodium hydroxide until the solution is again pink. Deduct a blank obtained by carrying a boron-free sample of titanium through the entire procedure.

RESULTS

The results obtained for boron in synthetic alloys prepared by adding standard boron solution to pure titanium metal are shown in Table I. The results obtained in the presence of possible interferences are shown in Table II. None of the elements found in commercial titanium alloys interferes with the method.

TABLE I

RESULTS FOR BORON IN SYNTHETIC TITANIUM ALLOYS

Boron added (%)	Average boron found (%)	Std dev. (%)	No. of determinations
0.025	0.025	0.002	5
0.050	0.049	0.002	5
0.125	0.126	0.002	5
0.50	0.50	0.008	5
1.00	0.99	0.007	5

TABLE II

RESULTS FOR BORON IN TITANIUM ALLOYS IN THE PRESENCE OF POSSIBLE INTERFERENCES (2-gram sample)

Element added	Amount added (%)	Added as	Boron added (%)	Boron found (%)
Tungsten	5.0	$Na_2WO_4.2H_2O$	0.00	0.00
,,	,,	,,	0.125	0.127

Element added	Amount added %	Added As	Boron added %	Boron found %
Molybdenum	10.0	MoO_3	0.00	0.00
,,	,,	,,	0.125	0.127
Silicon	5.0	$Na_2SiO_3 \cdot 9H_2O$	0.00	0.00
,,	5.0	,,	0.125	0.122
Phosphorus	1.0	Na_2HPO_4	0.00	0.00
,,	,,	,,	0.125	0.123
Iron	10.0	Metallic Fe	0.125	0.126
Chromium	10.0	$Cr_2(SO_4)_3$	0.125	0.122
Vanadium	5.0	$(VO)_2Cl_4$	0.125	0.127
Manganese	10.0	$MnSO_4 \cdot H_2O$	0.125	0.123
Aluminum	5.0	$Al_2(SO_4)_3 \cdot 18H_2O$	0.125	0.127
Copper	5.0	$CuSO_4 \cdot 5H_2O$	0.125	0.123
Nickel	5.0	$NiCl_2 \cdot 6H_2O$	0.125	0.126
Cobalt	5.0	$CoCl_2 \cdot 6H_2O$	0.125	0.123
Tin	5.0	$SnCl_2 \cdot 2H_2O$	0.125	0.123
Magnesium	5.0	$MgSO_4 \cdot 7H_2O$	0.125	0.126

SUMMARY

There is need for a rapid method for the determination of moderate amounts of boron in titanium alloys. In this paper a method is proposed which uses ion exchange. The method is applicable to titanium alloys containing 0.025 to 1 per cent. boron. One or two grams of the sample are dissolved in hydrochloric acid, and the titanium and boron are oxidized with nitric acid. The bulk of the titanium is removed by a cation exchanger. A calcium carbonate separation is made to remove the residual titanium and adjust the acidity. The boron is then titrated with sodium hydroxide, after the addition of mannitol. None of the elements found in commercial titanium alloys interferes with the method.

RÉSUMÉ

Une bonne méthode rapide de dosage de bore (en teneur relativement faible) dans les alliages de titane, faisant défaut, les auteurs ont mis au point un procédé par échange d'ions. Il est applicable aux alliages de titane renfermant 0.025 à 1% de bore. Un à deux grammes d'échantillon sont dissous dans l'acide chlorhydrique; le titane et le bore sont oxydés par l'acide nitrique. La presque totalité du titane est éliminée par un échangeur de cations. Une séparation au carbonate de calcium est ensuite effectuée pour éliminer le titane restant. Puis on ajuste l'acidité et on titre le bore par l'hydroxyde de sodium après addition de mannitol. Aucun des éléments présents dans les alliages de titane commerciaux ne gênent.

ZUSAMMENFASSUNG

Da eine schnelle zuverlässige Methode für die Bestimmung von Bor (bei relativ schwachem Gehalt) in Titanlegierungen fehlt, haben die Autoren ein Verfahren durch Ionenaustausch entwickelt. Es ist auf Legierungen des Titans anwendbar, welche 0.025 bis 1% Bor enthalten. Ein bis zwei Gramm der Substanz werden in Salzsäure gelöst; das Titan und das Bor werden mit Salpetersäure oxydiert. Das Titan wird fast quantitativ durch einen Kationenaustauscher eliminiert. Eine Abtrennung mit Calciumkarbonat wird anschliessend vorgenommen, um das verbleibende Titan zu eliminieren. Dann wird die vorgeschriebene Azidität herbeigeführt und man titriert das Bor mit Natronlauge, nachdem man Mannitol hinzugegeben hat. Kein Element, das in den handelsüblichen Titanlegierungen vorkommt stört die Methode.

References p. 238.

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THE DETERMINATION OF THE TOTAL ELECTROLYTE CONCENTRATION OF SUGAR PRODUCTS

by

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The ash-content of sugar products is widely accepted as an indication of the mineral constituents they contain.

As the chemical ash determination requires a great deal of care and considerable time, and is subject to considerable uncertainty (volatilization of ammonium and potassium salts, of nitrates and chlorides, conversion of organic acids to carbonates) it has been partly replaced — especially as a routine test in factory laboratories — by the electrical conductivity method as an indirect measure of the ash-content.

The conductivity is known to be correlated to the concentration of ionized salts present in an impure sugar solution, but the method shows several discrepancies, as compared with ash determinations, especially in the estimation of mineral matter in cane sugar.

The discrepancies are caused by the variability of composition of dissolved salts, and by the fact that the specific conductance is affected only by the concentration of ionized salts and not by those present in the water-insoluble portion of the sugar, whereas the chemical ash represents the sum of the total mineral matter.

This paper deals with a simple method of determining the total electrolyte content of sugar.

The determination is based on the fact that if a neutral solution containing several salts is passed through a hydrogen ion exchange column, the effluent contains a quantity of acid equivalent to the original salt content. By titration of the liberated acid, the total electrolyte content of the tested solution can be determined.

The presence of unknown acids in the solution, in addition to the mineral salts, requires a separate titration of the acid originally present and subtracting the value from the titration of the effluent of the exchange column.

The procedure has been employed previously, for the determination of total salt content in vegetable tanning liquors[1], calcium in sulphite cooking acid[2],

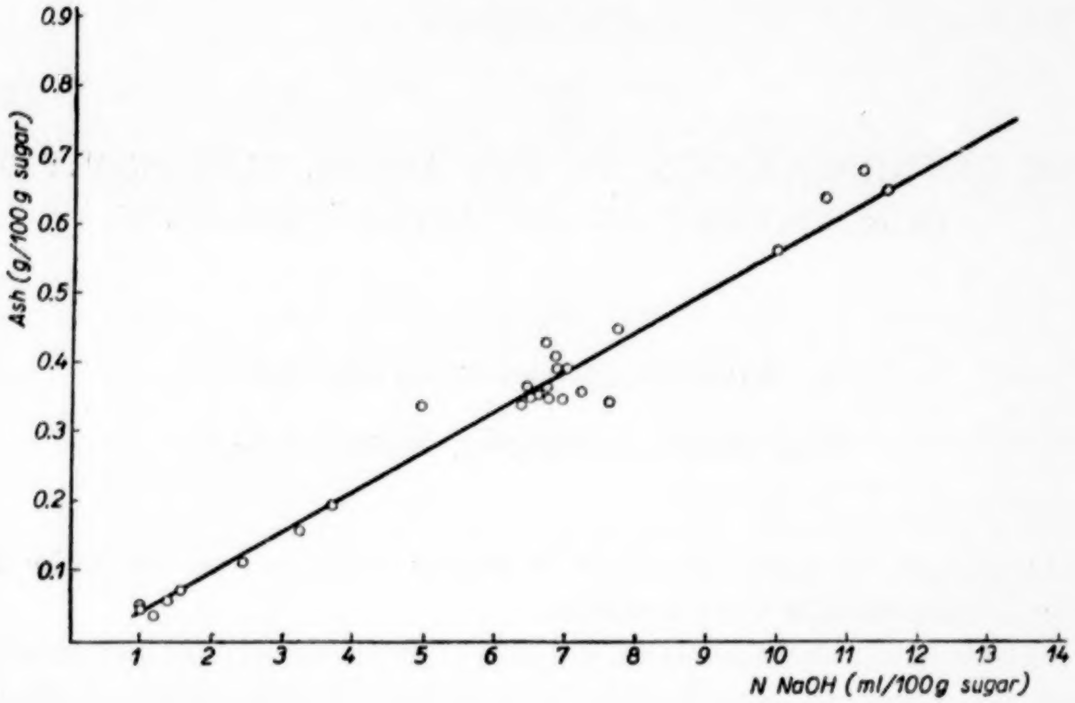

Fig. 1. Relation of ash to electrolyte content.

total electrolyte content of natural waters[3], water analysis[4] and total base of serum[5].

EXPERIMENTAL

Material

32 samples of brown cane sugar imported in this country during the years 1952-1954 were tested.

Preparation of column

25 g of analytical reagent grade Amberlite JR-120 cation exchange resin (a high capacity resin of nuclear sulphonic type — having a total exchange capacity of 4.2 milliequivalents per gram) were introduced into a graduated 100 ml glass column fitted with a tap. The dimensions of the resin column were 14 mm × 250 mm. The resin was supported on and covered with a layer of glass wool.

The resin was regenerated with 100 ml of a 10% hydrochloric acid solution and washed with distilled water until 50 ml of effluent required less than 0.05 ml of 0.1*N* sodium hydroxide for neutralization in the presence of phenolphthalein (2 drops of a 1 percent ethyl alcoholic solution).

The regenerating acid solution and distilled water were placed in a separatory funnel above the column and passed at a rate of 6-8 and 10-12 ml per minute respectively.

Procedure

20 g of brown sugar were dissolved in a 250 ml beaker, filtered through a rapid ashless filter paper (Schleicher and Schüll No. 589-1-H was used in our determinations) into a 250 ml volumetric flask. After filling to the mark and mixing, 100 ml of the solution were transferred to a 600 ml beaker, diluted to about 500 ml and after addition of 5-8 drops of phenolphthalein titrated with 0.1*N* sodium hydroxide from a semimicroburette, till appearance of a permanent pale pink colour.

Another 100 ml portion of the solution was passed through the prepared column at a rate of 6-8 ml per minute. The column was washed with distilled water until acid-free (about 500 ml of water were required). The effluent shows a limited decolourization of the sugar. After addition of phenolphthalein solution, the effluent was titrated with an 0.1*N* sodium hydroxide solution.

(*Note:* The dissolved sugar should not be kept for a long period, because of acidity increase in the original solution. No measurable increase in acidity was found on standing for 4 hours at room temperature.)

The number of ml of normal base required to neutralize the acid liberated by total electrolyte present in 100 g of sugar, was compared with the ash content (g in 100 gram sugar) of the tested samples.

The ash was determined by the A.O.A.C. method (Methods of Analysis A.O.A.C. 4th edition p. 465, 1935, method I) but the treatment with ammonium carbonate was deleted.

RESULTS

The graphical presentation of results is given in Fig. 1. A high factor of correlation — 0.92 — with the standard ash determination was found. The determinations made it possible to devise the simple formula of the type: $y = ax + b$ based on the linear relation between the ash and proposed electrolyte determination:

$$y = 0.05750\,x - 0.00893$$

whereas y = ash percentage

x = ml of normal base required for neutralization of acid liberated by electrolyte present in 100 g sugar.

Duplicate determinations agreed within less than 0.05 ml of 0.1*N* sodium hydroxide required for titration.

As the quantity of acid required for complete column regeneration is relatively large, and the time required for acid removal rather long, tests have been made to employ the prepared column for several determinations without intermittent regeneration.

5 tests on brown sugar samples having an 0.35% ash content could be made by this procedure; results agreed within 0.05 ml of 0.1*N* sodium hydroxide.

(The number of tests that can be made depends on the column exchange capacity; total content, composition and concentration of electrolyte in tested sample; rate of exchange, height of column etc.).

REMARKS AND LIMITATIONS

The method proposed for evaluation of ash is based on the assumption that the mineral matters which comprise the true ash-content of sugar are water-soluble salts, the mineral content of the water-insoluble portion is therefore undetermined.

The ash constituents of cane sugar vary in cane grown in different countries and even in different places in the same country. The results presented in this paper are based on testing samples of cane sugar from various countries. It is assumed that even a higher factor of correlation can be found on testing samples of relatively constant ash composition.

On the other hand (in control work) the quantity of acid liberated by a unit quantity of sugar may be used for evaluation of the product, without conversion to ash percentage.

The negative sign of the constant b is attributed to the adsorption of various organic non-sugar constituents present in raw sugar, by the ion exchange column. (As the quantity of organic non-sugars in refined sugar is negligible no exchange of ions by such substances was found on testing 12 samples of white commercial sugar.)

Notwithstanding these limitations the proposed method offers advantages of speed (the determination can be completed within one hour), simplicity and relative precision.

The method requires very simple laboratory equipment and little technical skill. The procedure is applicable to routine analysis and enables a number of tests to be carried out concurrently.

The proposed determination determines the water-soluble electrolyte content (which is known to retard the sugar crystallization) and enables the mean equivalent weight of water-soluble salts present in sugar products to be determined — by comparison of the quantity of liberated acid with the chemical ash.

The latter procedure may, eventually, be employed to determine the origin of sugar or fluctuations in ash composition.

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SUMMARY

A simple method for determining the total electrolyte content of impure sugar solutions is presented. The method is based on passing the dissolved tested sample through a column of a cation exchanger (hydrogen form of nuclear sulphonic acid resin) and titrating the resulting solution with standard alkali solution. A high coefficient of correlation was found between the proposed method and ash determination. An equation has been established by which the ash may be calculated with sufficient accuracy for practical purposes.

RÉSUMÉ

Les auteurs proposent une méthode pour la détermination de la teneur en électrolytes des solutions de sucre. Elle consiste à faire passer la solution à analyser à travers une colonne d'échangeurs de cations (forme hydrogénée d'une résine sulfonée); puis on titre la solution résultante par une solution étalon d'hydroxyde alcalin. Les valeurs ainsi obtenues sont en corrélation avec celles obtenues par la détermination des cendres. Une équation a été établie pour permettre de calculer la teneur en cendres avec une précision suffisante pour les besoins de la pratique.

ZUSAMMENFASSUNG

Die Autoren schlagen eine Methode vor für die Bestimmung des Gehaltes an Elektrolyten von Zuckerlösungen. Bei diesem Verfahren wird die zu untersuchende Lösung durch ein Rohr geleitet, welches Kationenaustauscher enthält (hydrogenierte Form eines sulfonierten Harzes); dann wird die so behandelte Lösung mit einer Alkalilösung titriert. Die so erhaltenen Werte sind in einem bestimmten Verhältnis zu denjenigen, welche man durch die Bestimmung der Asche erhält. Es wurde eine Gleichung ermittelt, um den Gehalt an Asche mit einer für praktische Zwecke genügenden Präzision zu errechnen.

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SPECTROPHOTOMETRIC METHOD FOR THE ESTIMATION OF AMMONIUM ACETATE WITH SENSITIZED SCHIFF'S REAGENT

by

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Schiff's reagent has been successfully utilized for both qualitative and quantitative estimation of aldehydes by previous workers[1,2]. The reaction between aldehyde and Schiff's reagent has been shown by HOFFPAUIR *et al.*[3] to be sensitized by acetone and other ketones. TOBIE[4] has observed that sensitization of Schiff's reagent can be effected by holding the SO_2 content to a minimum and also suggested a method for the preparation of sensitized Schiff's reagent. He has used it for the quantitative estimation of aldehydes and also for qualitative analysis of free aldehydic groups in simple aldoses.

Even the sensitized Schiff's reagent contains some excess SO_2 over the theoretical quantity, calculated from the probable formula suggested for the colourless Schiff's reagent by WIELAND[5]. Alkali brings about the colouration of the reagent by neutralizing both excess SO_2 and SO_2 in loose combination with the fuchsin molecule; but a large excess of alkali renders the dye colourless with the formation of carbinol bases[6]. Thus with the proper control of the alkali content, the colour can be restored to the desired extent.

SO_2 content may be adjusted in another way, *viz.* by the addition of the salt of an acid weaker than H_2SO_3, *e.g.* ammonium acetate; the latter would enter into a displacement reaction, as a result of which the SO_2 content will decrease and the colour of the sensitized Schiff's reagent will be restored. The intensity of the colour formed in this manner is expected to depend on the concentration of ammonium acetate. This principle has been utilized, perhaps for the first time, for the estimation of ammonium acetate with the help of sensitized Schiff's reagent.

EXPERIMENTAL

A B.D.H. sample of fuchsin was purified by repeated crystallization before use. SO_2 used was freshly prepared and the other chemicals were of reagent quality.

Sensitized Schiff's reagent was prepared according to the method described by TOBIE[4]. 0.5 g of fuchsin was decolourized by the calculated amount of SO_2 so as to maintain 1 g of SO_2 per litre and the volume was made up to 1000 ml. On keeping the solution overnight, a light yellow colour persisted, which was removed by the minimum quantity of activated charcoal to give a perfectly colourless solution. Three sets of sensitized Schiffs' reagent containing varying quantities of SO_2 (1 g, 2 g, 3 g/litre) were similarly prepared.

Both fuchsin solution and the coloured solution obtained by the interaction of sensitized Schiff's reagent and ammonium acetate were analysed throughout the entire visible wavelength, ranging from 480-800 mμ with the help of Beckman Spectrophotometer (Model D.U.) at a slit width of 0.04 mm. The optical density versus wavelength curves in both the cases were found to show peaks at the same wavelength, *viz.* 535 mμ. It is therefore quite probable that, unlike the Schiff's aldehyde compounds[5], ammonium acetate simply restores the colour of fuchsin itself. So in all subsequent readings 535 mμ was chosen as the characteristic wavelength for the coloured solution obtained from ammonium acetate and sensitized Schiff's reagent.

Preliminary experiments, carried out with sensitized Schiff's reagent and ammonium acetate showed that the restoration of colour could be effected even in absence of air, *e.g.* in an atmosphere of N_2 or CO_2. Oxygen, therefore, plays no part in the aforesaid reaction. It was also observed that the restoration of colour which proceeded with time was well marked when a slight excess of ammonium acetate, needed for the neutralization of free SO_2 in the reagent, was added. Thus for comparative purposes all optical density readings could be expediently taken just after 15 minutes (fixed arbitrarily) of mixing the reagents.

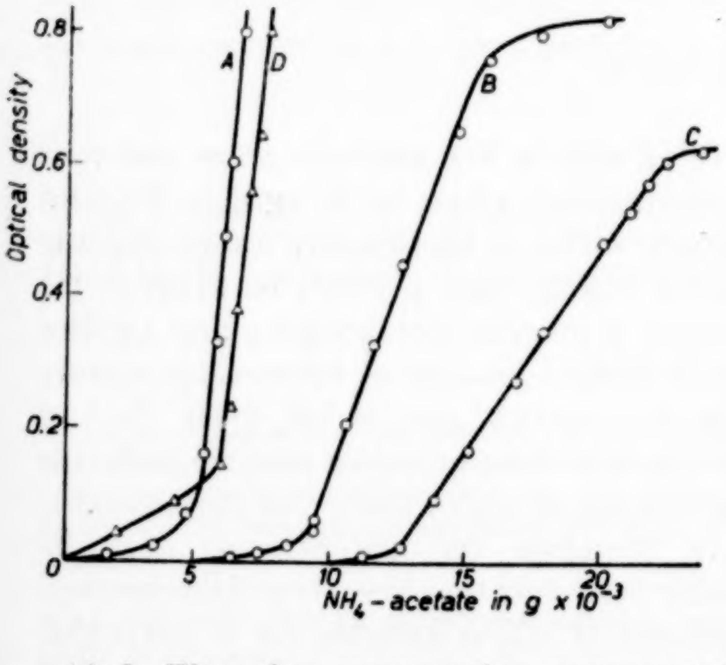

Fig. 1.
Curve:— A-With Schiff's 1 g SO_2/litre
Curve B-With Schiff's 2 g SO_2/litre
Curve C-With Schiff's 3 g SO_2/litre
Curve D-With Schiff's 2 g SO_2/litre containing 1 ml acetone per 5 ml reagent.

To draw a standard curve between concentration of ammonium acetate versus optical density the following procedure was adopted. To a series of test tubes each containing 5 ml of sensitized Schiff's reagent was added 1 ml of solutions of

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ammonium acetate of varying concentrations. A suitable time interval was kept between any two additions. The contents were mixed well and the optical densities measured at 535 mμ exactly after 15 minutes. A standard curve obtained from a particular set of sensitized Schiff's reagent corresponds to only a limited range of estimable ammonium acetate. So three standard curves with three sets of Schiff's reagent having varying SO_2 contents were drawn following the same procedure. The graphs are presented in Fig. 1.

Several experiments were carried out to determine the strengths of an ammonium acetate solution following the above procedure. The concentrations obtained from the standard curves were within 1% of that value determined by a standard method. The results are tabulated below.

TABLE I

ESTIMATION OF AMMONIUM ACETATE IN g BY ALKALI DISTILLATION (A′) AND BY THE PROPOSED METHOD (B′)

	I	II	III	IV	V	VI
A′	0.00605	0.0069	0.0141	0.0144	0.0236	0.0104
B′	0.0061	0.0069	0.0141	0.0146	0.0233	0.0105

DISCUSSION

The standard curves obtained for three sets of SO_2 contents show different sensitivity ranges. Thus the reagents containing 1g/litre (A) or 2g/litre SO_2 and acetone (D) change the intensity of colour within a very narrow range and the colour throw is very abrupt. This sudden change may perhaps be utilized, for instance, for titration work. Those samples of reagent containing 2 g and 3 g/litre SO_2 show the first colour change after a definite amount of ammonium acetate has been added. The latter depends on the concentration of SO_2 itself. Beyond this the colour throw is sharp and the optical density varies linearly with the concentration of ammonium acetate, which has an upper limit. For the quantitative estimation of ammonium acetate, therefore, its concentration must be adjusted so that it corresponds to the linear portion of the curve. It will be observed that a reagent containing a definite amount of SO_2 is suitable for a particular range of ammonium acetate concentration. Hence, the reagent should be selected from a knowledge of the approximate concentration of ammonium acetate to be estimated.

The slopes of the curves A, B and C may be taken as a measure of the sensitivity of the colour change. Thus a higher concentration of SO_2 makes the colour change less sensitive. For accurate work, therefore, the ammonium acetate solutions to be analysed should be suitably diluted so that its concentration lies on a standard curve of a satisfactory sensitivity.

It has been observed that the addition of acetone sensitize the Schiff's reagent[3]. In fact, standard curve drawn with varying amounts of ammonium acetate versus optical densities, observed with 5 ml Schiff's reagent (2 g SO_2/litre) containing 1 ml acetone, gives more or less identical curve with that obtained by Schiff's reagent having 1g SO_2/litre. The curve (D) with acetone is also presented for comparison. Thus a particular set a sensitized Schiff's reagent may be easily made more sensitive by the addition of appropriate amounts of acetone, rendering one set of sensitized Schiff's reagent useful for different ammonium acetate concentrations. The function of acetone is probably to react with a portion of the free SO_2 content and therefore it increases the sensitivity corresponding to a lower content of SO_2. Being more quick and sensitive this method is advantageous over the standard ones available for the estimation of ammonium salts.

The choice of the time lapse for recording of optical density is no doubt arbitrary, but it must be noted that if this is large the standard curves in some cases become less sensitive. For the optimum results, therefore, a lapse of 15 minutes has been found quite satisfactory.

It may be mentioned that by applying a similar procedure ammonium salt of other organic acids which are weaker than H_2SO_3 may be easily estimated. With the help of suitable standard curves alkali salt of such acids may also be estimable according to the above procedure.

ACKNOWLEDGEMENT

The authors wish to thank Dr. S.K. MUKHERJEE, D. Sc., Lecturer of Applied Chemistry, Calcutta University for his helpful criticism and also Dr. P. C. RAKSHIT, Head of the department of Chemistry, Presidency College for laboratory facilities.

SUMMARY

A spectrophotometric method has been described for the estimation of ammonium acetate with the help of sensitized Schiff's reagent.

1) Ammonium acetate restores the colour of fuchsin from the Schiff's reagent as shown by the same absorption maxima at 535 mμ of the coloured compound and fuchsin.

2) Standard curves of optical density versus concentration of ammonium acetate with different sets of sensitized Schiff's reagent having varying SO_2 contents have been presented.

3) There is a limit of ammonium acetate concentration beyond which the sensitivity considerably decreases.

4) Appropriate amounts of acetone along with a particular set of sensitized Schiff's reagent make the latter useful for different sensitive ranges of concentrations of ammonium acetate.

5) The method may be extended in its scope for the estimation of ammonium salts of other organic acids which are weaker than H_2SO_3.

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RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage de l'acétate d'ammonium au moyen du réactif de Schiff.

1) L'acétate d'ammonium régénère la coloration de la fuchsine du réactif de Schiff, avec une même absorption maximum à 535 mμ.

2) Les courbes étalon de la densité optique, obtenues pour une certaine concentration d'acétate d'ammonium en fonction de différentes quantités de réactif de Schiff (renfermant des teneurs variées de SO_2), ont été établies.

3) Il y a une limite de concentration d'acétate d'ammonium pour laquelle la sensibilité diminue considérablement.

4) Des quantités appropriées d'acétone peuvent permettre d'appliquer le réactif de Schiff à différentes concentrations d'acétate d'ammonium.

5) Cette méthode peut être étendue au dosage d'autres sels d'ammonium d'acides organiques, à condition que ces derniers soient plus faibles que SO_3H_2.

ZUSAMMENFASSUNG

Es wird eine spektrophometrische Methode beschrieben für die Bestimmung von Ammoniumacetat mit Hilfe des Schiffschen Reaktives.

1) Das Ammoniumacetat regeneriert die Farbe des Fuchsins vom Schiffschen Reaktiv, mit der gleichen maximalen Absorption bei 535 mμ.

2) Es wurden Eichkurven für die optische Dichte ausgearbeitet für eine bestimmte Konzentration von Ammoniumacetat in Funktion von verschiedenen Quantitäten des Schiffschen Reaktives (welche verschiedene Konzentrationen von SO_2 aufweisen).

3) Es besteht eine Grenzkonzentration für Ammoniumacetat, ab welcher die Sensibilität beträchtlich vermindert wird.

4) Durch angemessene Quantitäten von Aceton kann die Anwendbarkeit des Schiffschen Reaktives auf verschiedene Konzentrationen von Ammoniumacetat erweitert werden.

5) Diese Methode kann auch auf andere Ammoniumsalze organischer Säuren angewendet werden, unter der Bedingung, dass diese letzten schwächer sind als H_2SO_3.

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SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF THE RELATIVE STRENGTHS OF ORGANIC ACIDS WITH SENSITIZED SCHIFF'S REAGENT

by

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It has been demonstrated experimentally[1] that the intensity of colour developed by the addition of ammonium acetate to a sensitized Schiff's reagent[2] is a function, under proper conditions, of the concentration of ammonium salt, and as such a method has been suggested for the estimation of the latter. An enquiry into the mechanism indicates that the colour development is caused by the removal of SO_2 by means of the displacement reaction.

$$2CH_3COONH_4 + SO_2 + H_2O \rightleftarrows (NH_4)_2 SO_3 + 2CH_3COOH.$$

If this be so, ammonium acetate may be replaced by other ammonium salts of weak acids. Obviously, the acids should be weaker than sulphurous acid. It also follows from this that under similar conditions the intensity of colour developed may be taken as a relative measure of the strengths of the acids, since the extent of the removal of SO_2 will be determined by their strengths relative to sulphurous acid. The weaker the acid the greater the displacement of SO_2 and the greater the intensity of colour, so that the latter stands in an inverse relationship with the strengths of the acids. The experimental results obtained with oxalic, citric, *d*-tartaric, formic, lactic, succinic, acetic, butyric and propionic acids have been presented in this paper to substantiate the above suggestions.

EXPERIMENTAL

A B.D.H. sample of fuchsin was purified by repeated crystallization.

The other chemicals used were of reagent quality.

The sensitized Schiff's reagent was prepared according to TOBIE[2]. 0.5 g of fuchsin was decolourized by the calculated amount of H_2SO_3 solution so as to contain 2 g of SO_2/litre and the volume was made up to 1000 ml. The light yellow colour remaining after keeping the solution overnight was removed by treatment with the minimum amount of activated charcoal.

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Preliminary experiments showed that the coloured substance obtained by adding ammonium salts of the different acids to the sensitized Schiff's reagent possesses an absorption maxima at the same wavelength 535 mμ, which is characteristic of fuchsin itself. Optical density reading were therefore taken at 535 mμ. For comparative purposes the optical density readings, which vary with time, were recorded just after 15 minutes of mixing the reactants. The optical densities are, of course, comparable if any other period is chosen, say 30 minutes, 60 minutes or even few hours. The Beckman Spectrophotometer (Model DU) with a slit width of 0.04 mm was used for optical measurement.

The following is a typical set of experiments. Test tubes were arranged in series, each containing 5 ml of the sensitized Schiff's reagent. To each of the test tubes 1 ml of NH_4 salt of different acids having the same concentration (0.272*N*) was added. Optical densities were taken just after 15 minutes of mixing.

Air has very little influence on the reaction and hence no care was taken to exclude it. Optical densities along with other relevant data are presented in Table I. The dissociation constants have been taken from I.C.T.[3].

The relative strengths of the acids have been preferably calculated in terms of oxalic acid assuming it be 100% strong, so that

$$\text{strength of an acid} = \frac{100 \times \text{optical density with oxalic acid } (NH_4\text{ - salt})}{\text{optical density with the acid } (NH_4\text{ - salt})}$$

The results are given in the last column of the table.

TABLE I

Name of acid	Dissociation constant	Optical density of Schiff's with NH_4-salt	Relative strength
Oxalic	$6.5 \cdot 10^{-2}$	0.005	100
Citric	$8.0 \cdot 10^{-4}$	0.019	26.3
d_1-tartaric	$5.9 \cdot 10^{-4}$	0.027	18.52
Formic	$2.1 \cdot 10^{-4}$	0.0285	17.55
Lactic	$1.36 \cdot 10^{-4}$	0.037	13.52
Succinic	$6.7 \cdot 10^{-5}$	0.085	5.88
Acetic	$1.813 \cdot 10^{-5}$	0.298	1.68
n-Butyric	$1.5 \cdot 10^{-5}$	0.323	1.55
Propionic	$1.32 \cdot 10^{-5}$	0.337	1.48

DISCUSSION

It will be clear from the data that the dissociation constant varies inversely as the optical density. The acids have been arranged in the order of decreasing dissociation constants; the relative strengths of the acids also follow the same order.

As mentioned earlier, the choice of the appropriate concentration of the ammonium salts should be made so as to place the system in the sensitive region of the measurements. From the consideration of the sensitive regions in the optical density vs concentration curves of the individual ammonium salts, the best concentration suitable for all these ammonium salts was found to be 0.272*N*. It must, however, be pointed out that even at this concentration, the sensitivities of the different salts are not of the same order but it is good enough for purposes of comparison.

ACKNOWLEDGEMENT

Our thanks are due to Dr. S. K. MUKHERJEE D.Sc., Applied Chemistry, Calcutta University for his helpful criticism and to Prof. P. C. RAKSHIT, Presidency College, for his help and laboratory facilities.

SUMMARY

1. Ammonium salts of the weak acids, oxalic, citric, tartaric, formic, lactic, succinic, acetic, *n*-butyric and propionic bring colour to sensitized Schiff's reagent. The intensity of the colour thus produced stands in inverse relationship with the dissociation constants of these acids and hence of their strengths. The intensity of colour is dependent on the concentration of the ammonium salts and hence the concentration of the latter was adjusted to a suitable value, keeping in mind the range of the sensitivity of the reagent itself.

2. The colour produced by the different salts is the same as that of the solution. The probable mechanism appears to be that the ammonium salts react with SO_2 which displaces the acids from the salts. The greater the displacement the greater the intensity of colour and the weaker the acid.

RÉSUMÉ

1. Les sels d'ammonium des acides faibles suivants: oxalique, citrique, tartrique, formique, lactique, succinique, acétique, *n*-butyrique et propionique colorent le réactif de Schiff. L'intensité de la coloration produite est inversément proportionnelle aux constantes de dissociation de ces acides et par conséquent à leurs forces. L'intensité de la coloration dépend de la concentration des sels d'ammonium; la concentration de ces derniers est fixée en tenant compte de la sensibilité du réactif lui-même.

2. La coloration produite par ces différents sels est la même que celle de la fuchsine en solution. Il semble que le mécanisme probable est le suivant: le sel d'ammonium réagit avec SO_2 qui déplace les acides de leur sel. L'intensité de la coloration est d'autant plus grande que le déplacement est plus grand et que l'acide est plus faible.

ZUSAMMENFASSUNG

1. Die Ammoniumsalze folgender schwacher Säuren färben das Schiffsche Reaktiv: Oxal-, Zitronen-, Wein-, Ameisen-, Milch-, Bernstein-, Essig-, *n*-Butter- und Propionsäure. Die Intensität der Färbung ist umgekehrt proportional den Dissoziationskonstanten dieser Säuren und deshalb auch ihrer Stärke. Die Farbintensität hängt von der Konzentration an Ammoniumsalz ab; die Konzentration dieser Salze ist mit Rücksicht auf die Empfindlichkeit des Schiffschen Reaktives festgelegt.

2. Die Färbung, welche durch die verschiedenen Salze erzeugt wird, ist die

gleiche wie die des Fuchsins in Lösung. Es scheint, dass der wahrscheinliche Mechanismus der Reaktion wie folgt verläuft: Das Ammoniumsalz reagiert mit SO_2, welches die Säuren aus ihren Salzen umsetzt. Die Intensität der Färbung ist um so grösser, als die Umsetzung gross ist und als die Säure schwächer ist.

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THE HETEROMETRIC MICRO-DETERMINATION OF COPPER WITH QUINALDIC ACID IN THE PRESENCE OF FOREIGN METALS

by

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INTRODUCTION

The determination of copper with quinaldic acid has been investigated by various workers[1]. Most of the studies concern the gravimetric determination of copper in the presence of zinc, cadmium or iron. Because the metal quinaldate precipitates very slowly at room temperature, the gravimetric determination is carried out at a higher temperature. The determination of copper has also been studied by the amperometric method.

This paper deals with the heterometric determination of copper quinaldate at room temperature. Approximately 2 mg of copper in a volume of 10 ml was used for this determination. Owing to the insolubility of copper quinaldate, the precipitation begins almost immediately. However, the complete titration takes more time than is usually required by heterometric titrations. The maximum density values obtained are, in general, comparatively low. The sensitivity is much less than in the heterometric determination of copper with oxine. In spite of this, the use of quinaldic acid for the heterometric determination of copper may be of advantage in special cases. The advantages are as follows: the stability of the compound; the use of an aqueous solution; the *initial* precipitation occurs instantly, either in the absence or in the presence of foreign metals or complexing agents; the determination is possible in almost all cases; bivalent or trivalent metals may be present in large excesses; the presence of iron does not interfere if a complexing agent is used (in contrast to oxine). The maximum density values increase in special cases (iron or magnesium), making the determination more sensitive. Only in the presence of large excesses of zinc is the determination limited.

EXPERIMENTAL

The same apparatus and technique were used as in previous investigations[2]. The chemicals used were all either analytical reagents or chemically pure. The titrations were carried out at constant temperature 20° C (± 0.1) in order to obtain reproducibility of the maximum *values*. The latter could then be compared. The accuracy of the determination is entirely independent of the numerical values of the maximum and consequently is not dependent on the temperature during the titration. In all titrations with copper a blue filter was used and no other filters were used in the presence of excesses of coloured cations. Since these cations do not participate in the reaction, their colour has no influence on the results obtained.

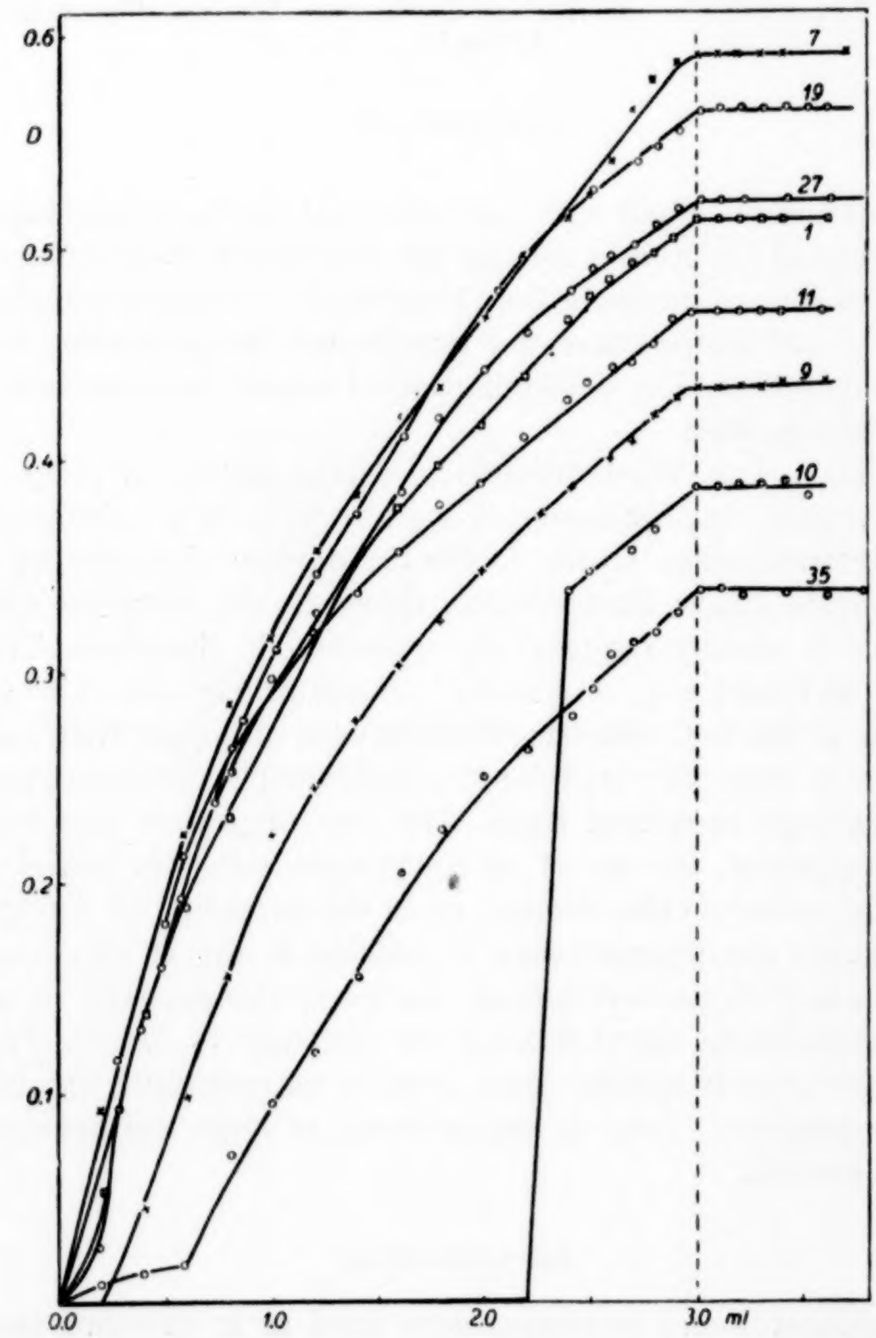

Fig. 1. Titration curves of copper sulphate with sodium quinaldate.

References p. 259.

TABLE I

General composition: 5 ml $CuSO_4$ 0.006M + 5 ml supplements + x ml Na-quinaldate 0.02M

Temp. 20°(±0.1°)C. Filter: blue. Content copper: 1.962 mg

Exp. number	Supplements	% Cu	x ml found	initial precip. at ml	Maxim. optic density	Approx. titration time in min	% Error
1	1 ml H_2SO_4 M + 4 ml H_2O		3.03	0.1	0.51	25	+1.0
2	1 " CH_3COOH M + 4 ml H_2O		2.98	0.0	0.53	24	—0.7
3	1 " " 0.1M + 4 ml H_2O		2.95	0.1	0.82	15	—1.6
4	1 " H_3PO_4 0.1N + 4 ml H_2O		3.00	0.1	0.70	15	0.0
5	1 " CH_3COOH M + 1 ml Na-acetate M + 3 ml H_2O		3.00	0.1	0.52	24	0.0
6	1 " Na_3-citrate 0.5M + 4 ml H_2O		2.97	0.4	0.42	20	—1.0
7	2 " Na_2-tartrate M + 3 " "		2.96	0.0	0.51	24	—1.3
8	1 " CH_3COOH M + 2 ml Na_2-tartrate M + 2 ml H_2O		2.96	0.0	0.53	23	—1.3
9	1 " " " + 1 " Na_3-citrate M + 3 " "		2.94	0.2	0.40	27	—2.0
10	1 " " " alc. + 4 ml alcohol		3.02	2.2	0.39	20	+0.7
11	1 " " " + 1 ml Na-acetate M + 1 ml Na_3-citrate 0.5M + 2 ml H_2O		2.98	0.1	0.47	24	—0.7
12	1 " " " + 2 ml $AlCl_3$ M + 2 ml H_2O	3.5	2.99	0.0	0.52	19	—0.3
13	1 " " " + 2 " $Cr(NO_3)_3$ M + 2 ml H_2O	1.8	2.98	0.0	0.41	41	—0.7
14	1 " " " + 1 " " " + 3 " "	3.6	3.00	0.0	0.39	42	0.0
15	1 " " " + 1 " $AlCl_3$ M + 2 ml Na_2-tartrate M + 1 ml H_2O	6.9	3.00	0.2	0.48	23	0.0
16	1 " " " + 1 " $Cr(NO_3)_3$ M + 2 ml Na_2-tartrate M + 1 ml H_2O	3.6	3.00	0.0	0.50	29	0.0
17	1 " " " + 1 " $FeCl_3$ M + 2 ml Na_2-tartrate M	3.4	3.03	0.1	0.82	20	+1.0
18	1 " " " + 1 " $AlCl_3$ 0.5M + 1 ml Na_3-citrate M + 2 ml H_2O	12.7	3.04	0.1	0.41	30	+1.3
19	1 " " " + 1 " $Cr(NO_3)_3$ 0.5M + 1 ml Na_3-citrate M + 2 ml H_2O	7.0	3.0	0.1	0.57	30	0.0
20	1 " " " + 1 " $FeCl_3$ 0.5M + 1 ml Na_3-citrate M + 2 ml H_2O	6.6	2.9	0.1	0.53	32	—3.3

RESULTS

Media

Table I and Figs. 1 and 2 give some results obtained in different media. Sensitivity to pH is not very pronounced (exp. 1, 2). Acetic acid and buffered acetate solutions give similar maximum density values (exp. 2, 5). The influence of the concentration of acetic acid can be seen if we compare exps. 2 and 3. Phosphoric acid may also be used (exp. 4). Considerable amounts of tartrate may be present either in the acetic acid solution or in the absence of this acid. Citrate may also be present in considerable amounts (exps. 6, 7, 8, 9, 11). Most of the titrations were carried out in 0.1*M* acetic acid solutions in the presence of excesses of foreign metals.

Determinations in the presence of bivalent cations

The results are given in Table II and Figs. 1 and 2. With the exception of barium,

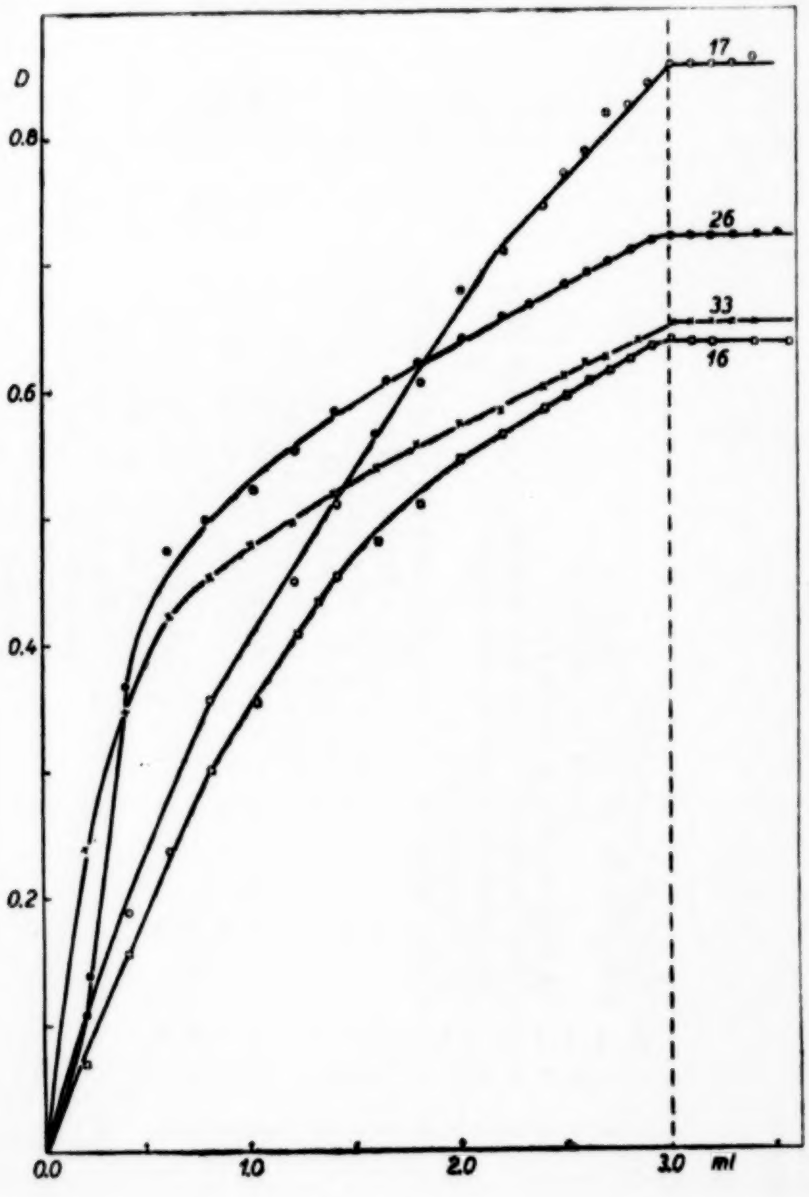

Fig. 2. Titration curves of copper sulphate with sodium quinaldate.

TABLE II

General composition: 5 ml $CuSO_4$ 0.006M + 1 ml CH_3COOH M + 4 ml supplements + x ml Na-quinaldate 0.02M Temp. 20°(±0.1°)C. Filter: blue. Content copper: 1.962 mg

Exp. number	Supplements	% Cu	x ml found	Initial precip. at ml	Maxim. optical density	Approx. titration time in min	% Error
21	2 ml $Ca(NO_3)_2$ M +2 ml H_2O	2.4	3.03	0.1	0.49	25	+1.0
22	1 ,, ,, ,, +3 ,, ,,	4.6	2.97	0.1	0.51	20	—1.0
23	2 ,, $BaCl_2$,, +2 ,, ,,	0.7	2.86	0.1	0.42	35	—4.4
24	1 ,, ,, ,, +3 ,, ,,	1.4	3.1	0.1	0.46	25	+3.3
25	2 ,, $MgSO_4$,, +2 ,, ,,	3.8	2.98	0.0	1.00	15	—0.7
26	1 ,, ,, ,, +3 ,, ,,	7.0	2.94	0.0	0.72	21	—2.0
27	1 ,, $MnSO_4$,, +3 ,, ,,	3.4	2.96	0.2	0.52	25	—1.3
28	2 ,, $NiCl_2$,, +2 ,, ,,	1.6	2.95	0.6	0.35	45	—1.7
29	1 ,, ,, ,, +3 ,, ,,	3.2	3.03	0.4	0.51	27	+1.0
30	2 ,, $Co(NO_3)_2$,, +2 ,, ,,	1.6	2.94	0.4	0.42	17	—2.0
31	1 ,, ,, ,, +3 ,, ,,	3.2	2.98	0.2	0.44	22	—0.7
32	2 ,, $CdSO_4$,, +2 ,, ,,	0.9	3.00	0.1	0.45	22	0.0
33	1 ,, ,, ,, +3 ,, ,,	1.7	3.04	0.1	0.65	15	+1.3
34	1 ,, $ZnSO_4$ 9.5N +1 ml Na_3-citrate M +2 ml H_2O		2.75	0.4	0.43	30	
35	1 ,, ,, 0.2 ,, +1 ,, ,, ,, +2 ,, ,,	13	3.00	0.6	0.34	38	0.0
36	1 ,, ,, 0.2 ,, +2 ,, Na_2-tartrate,, +1 ,, ,,	13	3.02	0.1	0.78	25	+0.7
37	1 ,, $Pb(NO_3)_2$ 0.5M +3 ml H_2O	1.9	3.00	0.0	0.69	26	0.0

the error in all cases was between zero and 2%. The maximum density values obtained were generally not affected by the presence of the foreign metal, nor by an increase in concentration. Noticeably higher density values were obtained in the presence of magnesium or lead, in the tartrate solution of zinc and perhaps also in the presence of cadmium (Table II, exps. 5, 6, 13, 16, 17).

Ca^{+2} (2.4% or 4.6% Cu). No influence due to Ca^{+2} was observed. The error was ± 1%.

Ba^{+2} (0.7% or 1.4% Cu). In the presence of higher concentrations of barium the determination became less certain.

Mg^{+2} (3.8% or 7% Cu). High maxima were obtained. The end-points were easily obtained from the intersection of two lines.

Mn^{+2} (3.4% Cu). The maximum point was obtained by the intersection of two lines.

Ni^{+2} (1.6% or 3.2% Cu). With less nickel the determination became easier. The end-points were obtained by the intersection of two lines.

Co^{+2} (1.6% or 3.2% Cu). No difficulties were encountered. Error 1-2%.

Cd^{+2} (0.9% or 1.7% Cu). The determination could be carried out in the absence of complexing agents. The error was between zero and 1.3%.

Zn^{+2} (13% Cu). With higher concentrations of zinc the end-point was unsure even in the presence of complexing agents. The end-point was obtained too soon (exp. 14) and the maximum values continued to rise. Zinc is probably coprecipitated. An unusually high maximum values was obtained in the presence of tartrate. This increases the sensitivity of the reaction. The error was small ($< 1\%$).

Pb^{+2} (1.9% Cu). Copper in this concentration could be accurately determined in acetic acid solution. With higher concentrations of lead a precipitate appeared before the beginning of the titration.

Determinations in the presence of trivalent cations

Table I and Figs. 1 and 2 present the composition and results of titrations in the presence of aluminum ($\gtrless$96%), chromium ($\gtrless$ 98%) or iron ($\gtrless$96%). All titrations were carried out in acetic acid solutions in the presence or absence of citrate or tartrate. In all cases the precipitation began immediately and the titrations lasted about 30 minutes. The error was generally between zero and 1.3%.

Al^{+3} ($\geqslant$ 3.5% Cu). No complexing agents were necessary. The determination could be carried out with the same success in tartrate or citrate solutions. The presence of aluminum probably did not influence the maximum density values.

Cr^{+3} ($\geqslant$ 1.8% Cu). Here, too, no complexing agent or special filter was necessary. The influence of chromium on the maximum density value was not marked. The error was less than 1%.

Fe^{+3} ($\geqslant$ 3.6% Cu). The titrations were carried out in the presence of either tartrate or citrate. In both cases a direct titration of copper could be carried out. In the presence of tartrate the maximum density values obtained were considerably increased. This is interesting as the sensitivity of the copper determination is thus increased. The error was 1%. The determination in the presence of tartrate is therefore preferable.

SUMMARY

1. During the heterometric determination of copper, bivalent cations may be present in solution in large excesses (>95%) and no complexing agents are necessary. In the presence of zinc, excesses of citrate of tartrate must be added. Error: 0—2 %.

2. Excesses of chromium or aluminum (>95%) are without effect. In the presence of an excess of iron (>95%) the determination is made by the addition of tartrate which increases the maximum density value obtained. Error: 0—3%.

RÉSUMÉ

1. Lors de la détermination hétérométrique du cuivre, certains cations bivalents peuvent être présents en grand excès (>95%) sans qu'il soit nécessaire d'ajouter un réactif complexant. En présence du zinc, il faudra ajouter un excès de citrate et de tartrate (erreur: 0—2 %).

2. Des fortes teneurs de chrome et d'aluminium (>95%) ne gênent pas. En présence de grandes quantités de fer (>95%) on ajoute du tartrate, il y a augmentation de la densité optique. (Erreur: 0—3%.)

ZUSAMMENFASSUNG

1. Bei der heterometrischen Bestimmung von Kupfer können gewisse Kationen in grossem Überschuss vorhanden sein (>95%), ohne dass die Zugabe eines komplexierenden Reaktives notwendig wird. Bei Gegenwart von Zink muss ein Überschuss an Citrat und Tartrat zugegeben werden (Fehler: 0—2%).

2. Die Anwesenheit von grossen Quantitäten von Chrom und Aluminium (>95%) stört nicht. Bei Gegenwart von grossen Quantitäten von Eisen (>95%) gibt man Tartrat zu; die optische Dichte wird dabei erhöht (Fehler: 0—3%).

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THE MICROCHEMICAL ELECTROLYTIC ANALYSIS OF ALLOYS IN HYDROCHLORIC ACID SOLUTIONS

II. WHITE METALS AND SOLDERS

by

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This work is a continuation of previous investigations undertaken in order to extend the use of alloy analysis by controlled potential electrodeposition [1,2,3,4]. Throughout, the apparatus and techniques employed were as described by **Sand and Lindsey.**

PRELIMINARY INVESTIGATIONS

White alloys vary considerably in composition, but most of the metals present are the same as in brasses or bronzes. Thus bearing metals may contain copper, antimony and tin with additionally lead and small amounts of zinc. The very different proportions of the constituent metals, however, make it necessary to modify the procedures described in Part I [4].

With white metals containing antimony, this latter metal is deposited with copper from hydrochloric acid solution and the mixed deposit is weighed. The mixed deposit is then redissolved in a mixture of nitric and hydrofluoric acids with a slight excess of potassium dichromate and copper alone deposited as was previously described[3]. The amount of antimony present is given by the difference between the two weights. Deposition of tin and lead together and of zinc afterwards (when present) is performed as was described for brasses and bronzes, but there is less difficulty in getting good deposits of zinc with the smaller quantities of this metal found in white metals. If desired, the mixed lead and tin deposits may be redissolved in nitric and hydrofluoric acids and the lead deposited as dioxide as described in the method for solders.

METHOD FOR WHITE METALS

The alloy (usually 5 to 20 mg) is dissolved in hydrochloric acid in an electrolysis tube with addition of small quantities of potassium chlorate and evaporated to small bulk in a waterbath. To the solution 1½ ml of hydrochloric acid and 4 drops of hydrazine hydrate (50%) are added. The solution is heated to 80° in a waterbath, stirred with hydrogen or nitrogen and the applied voltage raised until deposition is proceeding at a suitable rate (0.75 V). The time of electrolysis is about 20 minutes. The voltage is kept constant until the current has fallen to one tenth of its original value, then increased by about 0.05 V and continued until the current falls again. Washing, separation and drying of the electrode is carried out as previously described and the electrode is weighed.

The cathode is replaced in the apparatus and with the voltage reduced to zero, another electrolysis tube containing 7 drops of concentrated nitric acid and 2 drops of 40% hydrofluoric acid in sufficient water to cover the electrodes is raised from below. The solution is heated and potassium dichromate solution (10 per cent) added drop by drop until the yellow colour persists and all the deposit has dissolved from the cathode. Sufficient hydrazine hydrate is then added to destroy the colour and to leave an excess of three drops. Electrolysis of the solution at 0.7 volt for 10 minutes gives complete deposition of copper which is then weighed. The antimony is obtained by difference.

Tin is determined in the residual solution in a manner exactly as described previously for bronzes[4]. Lead, if present, is weighed with the tin.

Zinc, often present in such small amounts as to be of little interest in this type of analysis, may, however, be determined as was described previously[4].

Results of white metal analyses

Typical analyses of an alloy containing 4.30% copper, 7.45% antimony, 83.7% tin, 4.15% lead and 0.4% zinc are shown in Table I.

TABLE I

Wt. alloy used	Wt. Cu calculated	Wt. Cu obtained	Wt. Sb calculated	Wt. Sb obtained by difference	Wt. Sn & Pb calculated	Wt. Sn & Pb obtained
mg	mg	mg	mg	mg	mg	mg
6.18	0.26	0.26	0.46	0.46	5.43	4.39
9.02	0.39	0.39	0.67	0.67	7.98	7.96
8.16	0.35	0.36	0.61	0.60	7.17	7.15
7.40	0.32	0.32	0.55	0.55	6.50	6.45
11.97	0.51	0.50	0.89	0.90	10.51	10.50
6.62	0.29	0.28	0.49	0.47	0.82	5.77
8.48	0.36	0.36	0.63	0.63	7.45	7.47
6.54	0.29	0.29	0.49	0.48	5.75	5.70
19.55	0.84	0.85	1.46	1.44	17.17	17.23

METHOD FOR SOLDERS

Solders containing lead and tin with but traces of other metals can be examined by one or two procedures. Firstly, the alloy may be dissolved in hydrochloric acid with the aid of chlorate and both metals deposited as described previously. The lead and tin are weighed together and lead then determined as dioxide after redissolving the deposit. Alternatively the alloy may be dissolved in 3 ml concentrated nitric acid with 7 drops of 40% hydrofluoric acid present in order to keep the tin in solution. The solution is heated to boiling and electrolysed at the boiling point with the inner electrode as anode for ten minutes at 1.0 V. The lead is then present as dioxide on the anode. The electrolysis tube is replaced by another containing 2 ml nitric acid and 5 drops of 40 per cent. hydrofluoric acid in enough water to cover the electrodes. The deposit is dissolved off by bringing the solution to boiling and reversing the current. Upon making the inner electrode the anode once more, the deposition is repeated as before, the solution cooled and the deposit separated and washing in the usual manner. The lead dioxide deposit is weighed and the factor 0.860 employed for converting the weight to that of the metal.

Results for solder analyses

Typical analyses are given in Table II for a solder contains 62.0% lead and 37.9% tin and in Table III for a solder containing 60.1% lead and 37.6% tin.

TABLE II

Wt. alloy used mg	Wt. Pb calculated mg	Wt. PbO_2 obtained mg	Equivalent wt. of Pb mg	Wt. Sn calculated mg	Wt. Sn obtained by difference mg
12.19	7.55	8.75	7.53	4.61	4.66
8.65	5.36	6.25	5.37	3.28	3.28
7.27	4.51	5.24	4.51	2.75	2.76
5.11	3.17	3.66	3.15	1.94	1.96
9.23	5.71	6.62	5.70	3.50	3.53
4.67	2.89	3.35	2.88	1.77	1.79

TABLE III

Wt. alloy used mg	Wt. Pb calculated mg	Wt. PbO_2 obtained mg	Equivalent Wt. of Pb mg	Wt. Sn calculated mg	Wt. Sn obtained by difference mg
22.30	13.40	15.59	13.41	8.83	8.89
8.95	5.38	6.24	5.37	3.54	3.58
4.51	2.71	3.14	2.70	1.78	1.81
7.77	4.66	5.39	4.64	3.07	3.13
7.55	4.53	5.26	4.53	2.98	3.02
6.48	3.89	4.55	3.91	2.56	2.57
8.64	5.20	6.05	5.21	3.42	3.43
6.69	4.02	4.67	4.02	2.65	2.67
4.48	2.69	3.11	2.68	1.77	1.80
5.44	3.27	3.80	3.27	2.15	2.17

References p. 263.

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SUMMARY

The microchemical electrolytic analysis of alloys employing the methods of SAND AND LINDSEY for potential control have been extended to include white metals and solders. The methods, employing from 5 to 20 milligrams of material, may be completed in about 2 hours (excluding the time necessary to bring the sample into solution) and are especially useful in circumstances where only a few milligrams of sample are available.

RÉSUMÉ

Les méthodes d'analyse électrolytique microchimique d'alliages, utilisant les procédés de SAND ET LINDSEY (potentiel contrôlé) ont été appliquées aux analyses des métaux blancs et des soudures. Ces méthodes, utilisant 5 à 20 mg d'alliage, peuvent être effectuées en 2 heures environ (sans compter le temps nécessaire pour la mise en solution de l'échantillon); elles sont particulièrement utiles lorsqu'on ne dispose que de quelques milligrammes d'alliage.

ZUSAMMENFASSUNG

Die mikroelektrolytischen Analysenmethoden von Metallegierungen, die auf dem Prinzip von SAND UND LINDSEY beruhen (kontrollierte Potentiale), wurden auf die Analysen von Weissmetallen und Lötmetallen angewendet. Diese Methoden, die 5 bis 20 mg Legierung benötigen, können in ungefähr 2 Stunden ausgeführt werden (die Zeit für die Auflösung des Musters nicht gerechnet). Die Methoden sind besonders vorteilhaft, wenn man nur über einige Milligramme der Legierung verfügt.

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HIGH FREQUENCY TITRATIONS INVOLVING CHELATION WITH ETHYLENEDIAMINETETRA-ACETIC ACID

I. CHELATION STUDIES

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High frequency titrations hold considerable promise as a means of studying complexation. This is especially true where colorless systems must be studied or where delicately poised systems are encountered and various chemical and electrode reactions would be likely to shift the equilibria involved. Other investigators have used high frequency titrations to study complex formation[1,2,3,4] but the studies reported to date have been limited to the use of high frequency titrimeters for following direct titrations involving the metal ions and the complexing addenda. Such an approach can give valuable information where strong coordination tendencies are encountered and distinct breaks in the titration curve are obtained. Very often, however, the curves are complicated and difficult to interpret due to the sensitivity of high frequency methods to external factors and small changes in the chemical system under study.

The present work represents one part of a series of studies initiated for the purpose of developing new applications of high frequency measurements (Oscillometry), especially for studying coordination phenomena and compleximetric titrations. Studies of ethylenediaminetetra-acetic acid and its analytical applications were begun, partly because sufficient corroborative information is already recorded from investigations made using other approaches and partly because it was felt that the applications of this complexing reagent could be improved and extended in many cases by utilizing the sensitivity and versatility of the Oscillometer.

Ethylenediaminetetra-acetic acid is one of the strongest and most generally applicable chelating agents known. Numerous analytical applications have been made, usually based either on the measurement of liberated hydrogen ions resulting from chelation or on the direct measurement of the compleximetric reactions themselves. In the first type of determination, hydrogen ions liberated as a result of chelation cause a drop in pH of the solution.

$$H_4Y^{**} + M^{II}X^{-2} \rightarrow 2H^+ + X^{-2} + H_2(M^{II}Y)$$

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** Ethylenediaminetetra-acetic acid will be designated hereafter as H_4Y.

By means of suitable acid-base indicators or through the application of potentiometric methods, the displaced hydrogen ions can be titrated using standard base. The second approach depends on the use of ethylenediaminetetraacetic acid, or one of its salts, for the direct titration of metal ions at fixed hydrogen ion concentrations. Stoichiometric end-points are usually indicated by potentiometric, amperometric, or spectrophotometric means or by internal indicators which form colored, weakly bound complexes with the ion being titrated[5, 6, 7, 8].

High frequency oscillators possess obvious advantages where direct compleximetric titrations are to be followed because they are almost universally applicable, being both independent of electrode reactions and the necessity of having color systems. Furthermore, high frequency titrimeters serve admirably in following acid-base titrations and consequently are well suited for use in studies employing hydrogen liberation approaches.

EXPERIMENTAL

Reagents

All chemicals used were of C.P. or reagent grade.

Apparatus

The high frequency oscillator used was the Sargent Model V Oscillometer. A Beckman Model G pH meter was employed for measuring hydrogen ion concentrations.

Neutralizations of ethylenediaminetetra-acetic acid

The acidic character of ethylenediaminetetra-acetic acid was investigated by titration with various hydroxides.

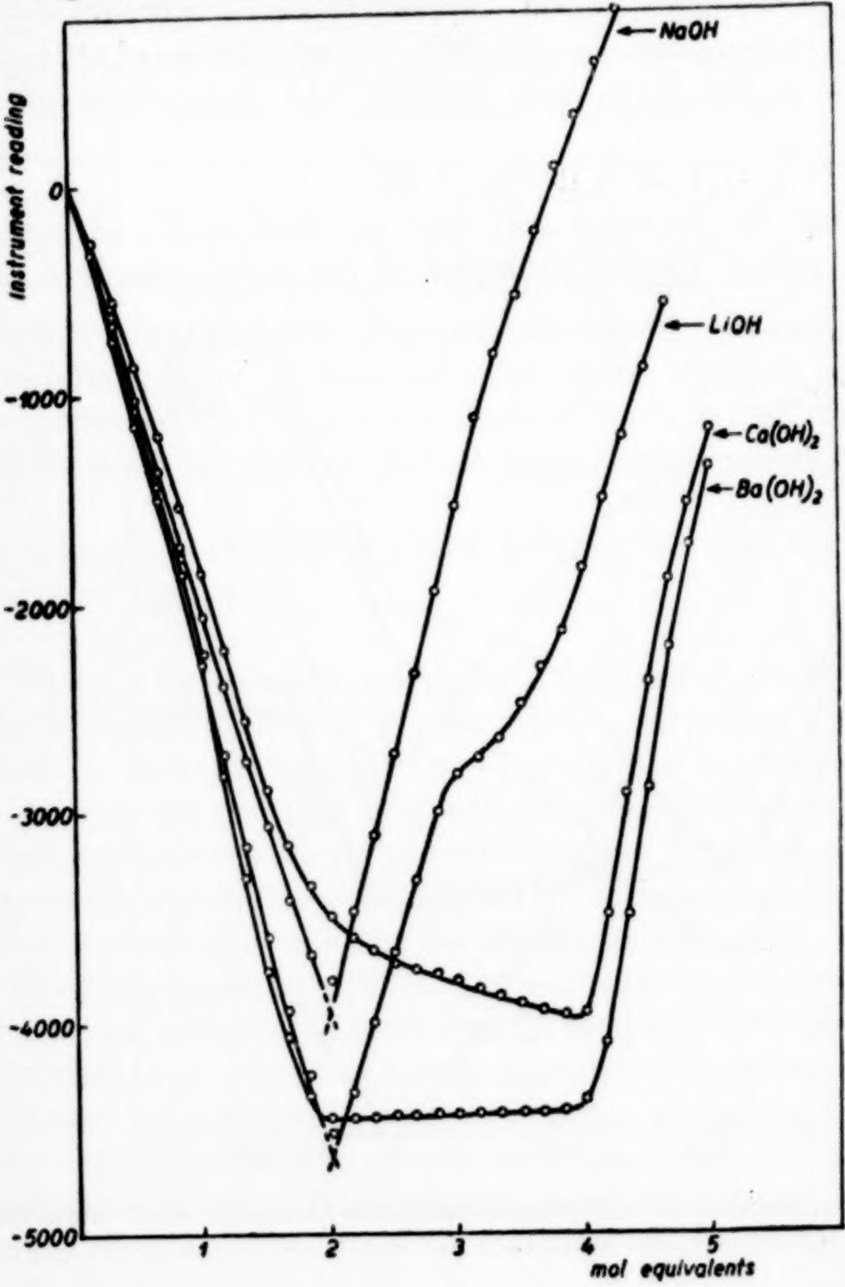

Fig. 1. Titrations of ethylenediaminetetra-acetic acid with various bases.

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One hundred ml portions of 1/1000M solutions ethylenediaminetetra-acetic acid was titrated with 1/30M solutions of lithium and sodium hydroxides and 1/60M solutions of barium and calcium hydroxides. Typical titration curves are shown in Fig. 1. In all cases distinct breaks occur at 2 mol equivalents of base indicating the neutralization of the acid with formation of the dibasic salt. In the case of barium and calcium hydroxides a second distinct break appears at 4 mol equivalents indicating the chelation of the metal ions, the shape of the curves showing a strong tendency toward coordination. The curve for the lithium hydroxide titration is of interest because of the distinct break between 3 and 4 mol equivalents indicating a weak tendency toward coordination.

Sodium hydroxide titrations of equimolar mixtures of ethylenediaminetetra-acetic acid and metal salts

When equimolar amounts of cobalt, nickel, copper(II), zinc, cadmium, lead, manganese (II), iron (III) and aluminum were added to 100 ml portions of 1/1000M ethylenediaminetetra-acetic acid chelation was found to take place according to the general reaction,

$$M^{+2} + H_4Y \rightarrow H_2(M^{II}Y) + 2H^+$$

This was shown by titrating the liberated acid with standard base and noting the shape of the titration curve. Typical examples of the curves obtained are

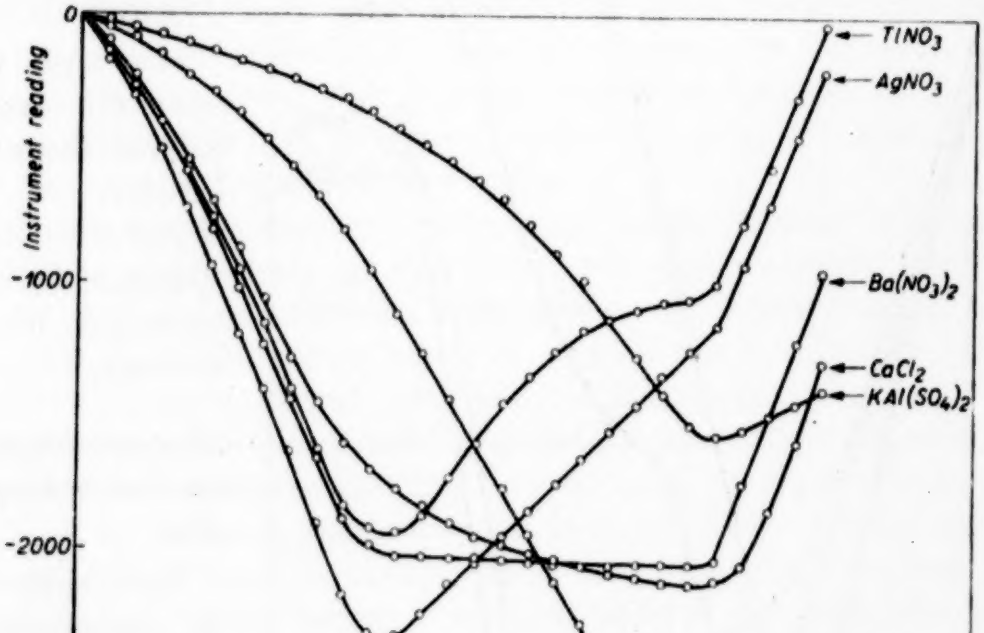

Fig. 2. Sodium hydroxide titrations of ethylenediaminetetra-acetic acid with the coexistence of equimolar amounts of metal salts.

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those of zinc and aluminum as illustrated in Fig. 2. It is to be noted that the curves drop smoothly to the inflection points which occur at a position indicating the liberation of 4 mol equivalents of hydrogen ion. The curves indicate that these metals have strong chelation tendencies, even in acidic solution.

Similar studies made with thallium(I) and silver also showed the final liberation of 4 mol equivalents of hydrogen ion, but the nature of the reaction was found to be distinctly different. As shown in Fig. 2, the titration curves indicate that normal neutralization (two hydrogens) of the acid first takes place. Then after the dibasic acid is formed and a higher pH is obtained, chelate formation is encountered and the final two hydrogens of the acid are replaced as shown by the break in the titration curve at 4 mol equivalents of added base. The indications are that the chelates formed with these metals are not sufficiently stable to produce a reaction with the acid itself and in fact, occur only concurrently with the neutralization of the final two hydrogens. Thallium(I) is especially slow to coordinate, the reaction becoming apparent only after the third hydrogen has been neutralized.

Calcium, barium, strontium and magnesium occupy an intermediate position in regard to their coordination tendencies. The titration curve for barium (also strontium and magnesium) shows that chelation does not become of major importance until the first two hydrogens of the acid have been neutralized. At this point, however, stable complexes begin forming and the titration curve shows a level floor until the sharp break at 4 mol equivalents of hydrogen is reached. Calcium appears to form the most stable chelates within this group of metals as evidenced by the lack of a distinct break at the dihydrogen equivalence point which must be present when simple neutralization precedes chelation.

Determination of reacting ratios by means of high frequency titrations of liberated hydrogen ions

When a metal salt is added to a solution of ethylenediaminetetra-acetic acid, the liberated hydrogen should reach a maximum concentration at that point where a definite composition of chelate is obtained. Further addition of the metal salt beyond that required for chelation should not cause any appreciable change in hydrogen ion concentration. By following the release of hydrogen ions titrimetrically as the ratio of metal to coordinating addendum is varied, the chemical composition of the chelate should be indicated.

Both ethylenediaminetetra-acetic acid and its disodium salt were used in studies of reacting ratios with metal ions. In each measurement 100 ml of the addendum ($1/1000M$) was placed in a large titration cell together with a calculated amount of metal salt solution ($1/50M$). The ratios of metal salt to addendum were varied over wide ranges so as to encompass all possible stable configurations. The liberated hydrogen ions were titrated with standard sodium hydroxide and the titration curves examined to determine the ratio beyond which no change in horizontal position of the inflection point occurred with increasing ratios of reactants. With such an experimental approach, cobalt, nickel, zinc, copper(II), cadmium, lead, manganese(II), iron(III) and aluminum salts were found to yield curves of similar shape. The cobalt curve (Fig. 3) serves to illustrate this general case. As shown by these data, the addendum alone gives the anticipated inflection point at 2 mol equivalents of hydrogen ion. Upon the addition of cobalt chloride the break shifts progressively with increasing ratios of metal/addendum until a 1 to 1 ratio is obtained. At this ratio 4 mol equivalents of hydrogen have been released and the composition of the chelate salt is indicated to be $Na_2(CoY)$.

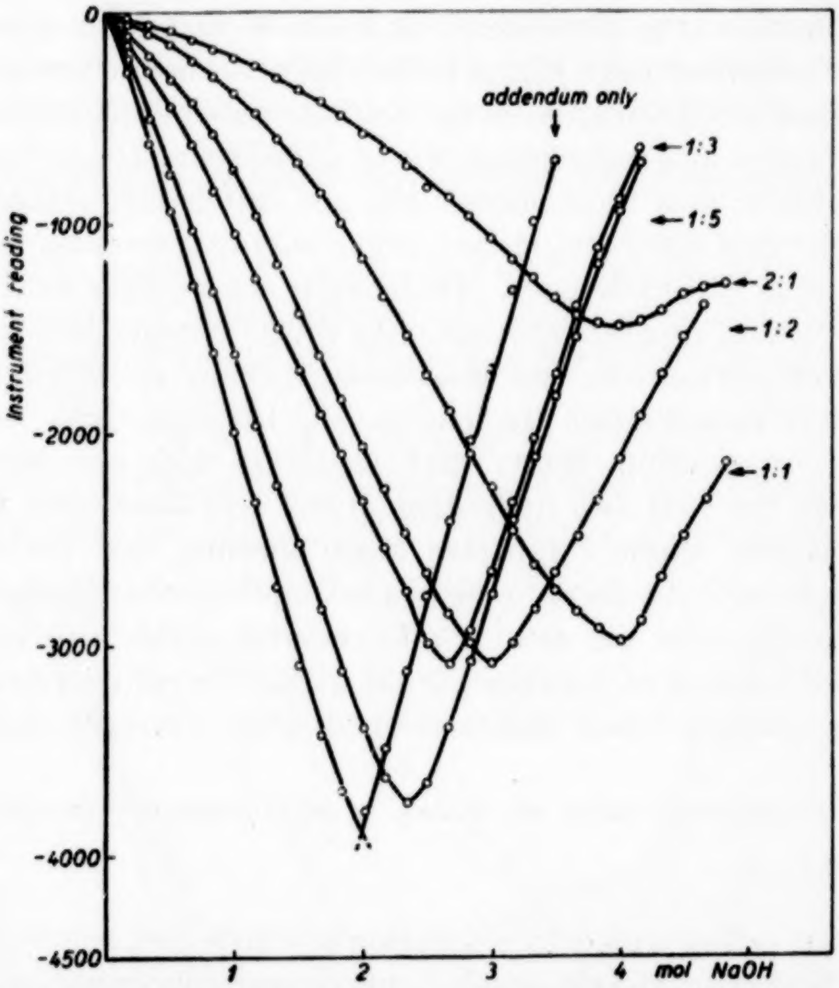

Fig. 3. Titrations of ethylenediaminetetra-acetic acid with the coexistence of cobalt chloride at various ratios of metal to addendum.

Metal salts such as iron (III) and aluminum give precipitates with concentrations of addendum in excess of 1 to 1 ratios and the titration curves obtained become ill-defined. All of the metals listed in this group, however, reached maxima indicating 1 to 1 ratios of metal to addendum.

Similar studies were made of alkaline earth metals, magnesium, silver and thallium (I), except that the disodium salt of ethylenediaminetetra-acetic acid was used as the complexing addendum. This modification was dictated by the

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fact, previously pointed out, that chelation does not take place with these metals until partial neutralization of the acid has taken place. Disodium ethylenediaminetetra-acetate gives no break upon titration with sodium hydroxide. Upon the addition of the alkaline earth metals, silver or thallium (I), titration curves are obtained which show the liberation of hydrogen ions. With small ratios of metal/addendum no well-defined breaks are obtained: when the ratio is increased, more distinct inflection points are evident and at ratios of 1 to 1 and 2 to 1 sharp breaks are obtained at 2 mol equivalents of sodium hydroxide, indicating the existence of stable chelates forming at equimolar ratios of reactants. Barium, strontium, calcium and magnesium gave curves of the type shown in Fig. 4. Titration curves for thallium(I) and silver differ from those of the other metals studied in that they do not show any sign of inflection until ratios of 1 to 1 are attained (Fig. 5). In the case of silver, the precipitation of brown silver oxide

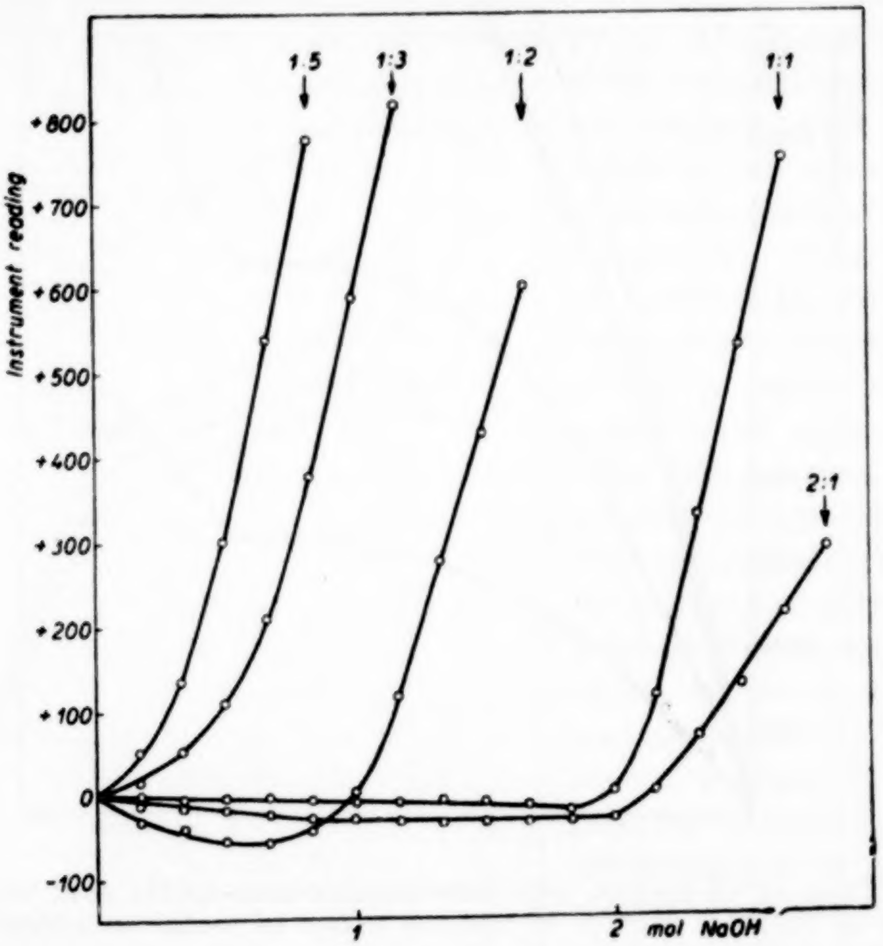

Fig. 4. Titrations of di-sodium ethylenediaminetetra-acetic acid with the coexistence of barium nitrate at various ratios of metal to addendum.

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masked the reaction when excess silver (*viz.* when ratios of silver addendum were 2 to 1 or greater) was present.

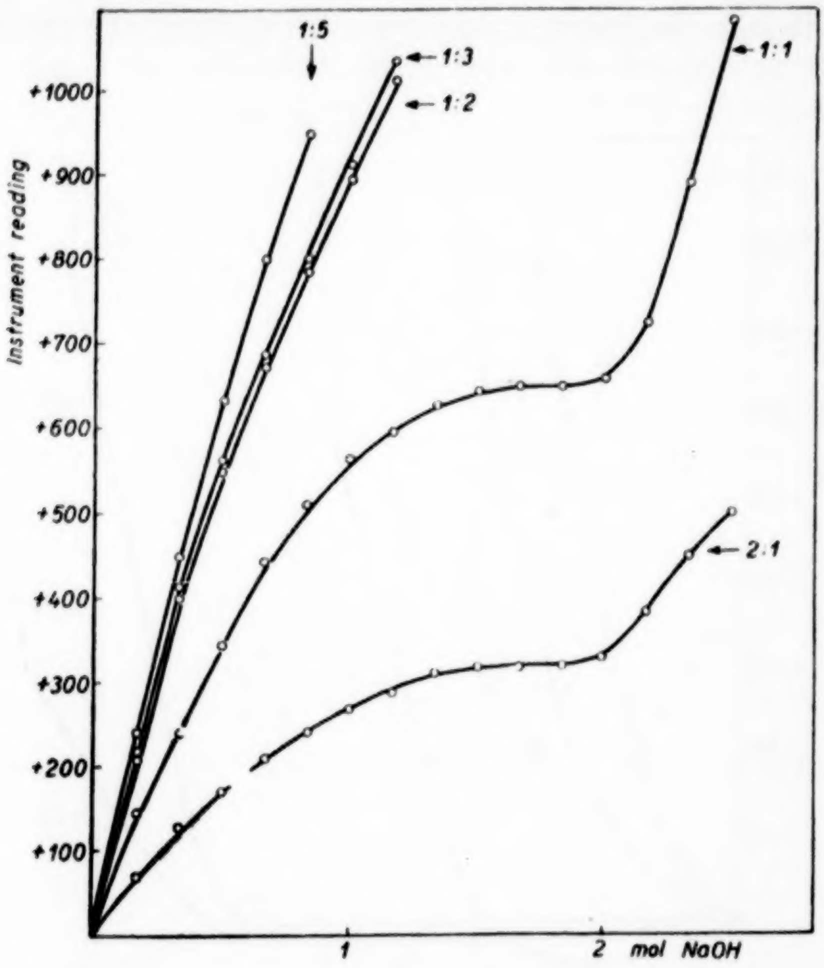

Fig. 5. Titrations of di-sodium ethylenediaminetetra-acetic acid with the coexistence of thallous nitrate at various ratios of metal to addendum.

Determination of reacting ratios by means of direct titrations

When a polyvalent metal salt is added to a solution of ethylenediaminetetra-acetic acid, chelate formation takes place. By adding the metal continuously or in small increments it should be possible to follow the resulting reactions by means of the oscillometer. In unbuffered solution the hydrogen ions liberated by chelation should increase the instrument's response. At the stoichiometric end-point no further hydrogen ions should be released: only uncombined (solvated) metal ions should be contributed by adding excess metal salt solution and a distinct inflection point should be indicated.

Experimental studies were designed to accommodate differences in reactivity of the various metals as established by hydrogen ion concentration. Because of stability differences at different acidities adjustment of pH was made, where

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necessary, so as to assure chelation. Acidities were adjusted by means of sodium hydroxide because unbuffered solutions were dictated on the basis of the experimental approach to be used. Cobalt, nickel, copper(II), cadmium, lead, zinc, manganese(II), iron (III), and aluminum were titrated directly into known volumes of ethylenediaminetetra-acetic acid, giving definitive results as illustrated in Fig. 6. The strong chelating tendencies of these metals is evidenced by their reactivity at the pH of the acid form of the addendum (pH 3). Alkali earth, magnesium, silver and thallium (I) salts give no response with titrations in solutions of either ethylenediaminetetraacetic acid or its di-sodium salt. Upon adjustment of acidities to pH 10, distinct breaks occur (Fig. 7) at mol ratios of 1 to 1. In the case of silver salts a break appears at a 1 to 1 ratio with a second break marked at ratios of approximately 2 to 1. This second inflection appears to be the result of silver oxide precipitation (Fig. 8). At pH 10, cobalt, nickel, copper (I), zinc, cadmium and manganese (II) yield titration curves showing two breaks at reacting ratios of 1 to 1 and approximately 2 to 1. Again, the second break coincides with precipitation and is not considered to be an indication of chelation. It is not a stoichiometric end-point and is shifted by changing amounts of precipitate. Iron (III) and aluminum give complicated titration curves at pH 10 and interpretation of the various inflection points is not now feasible.

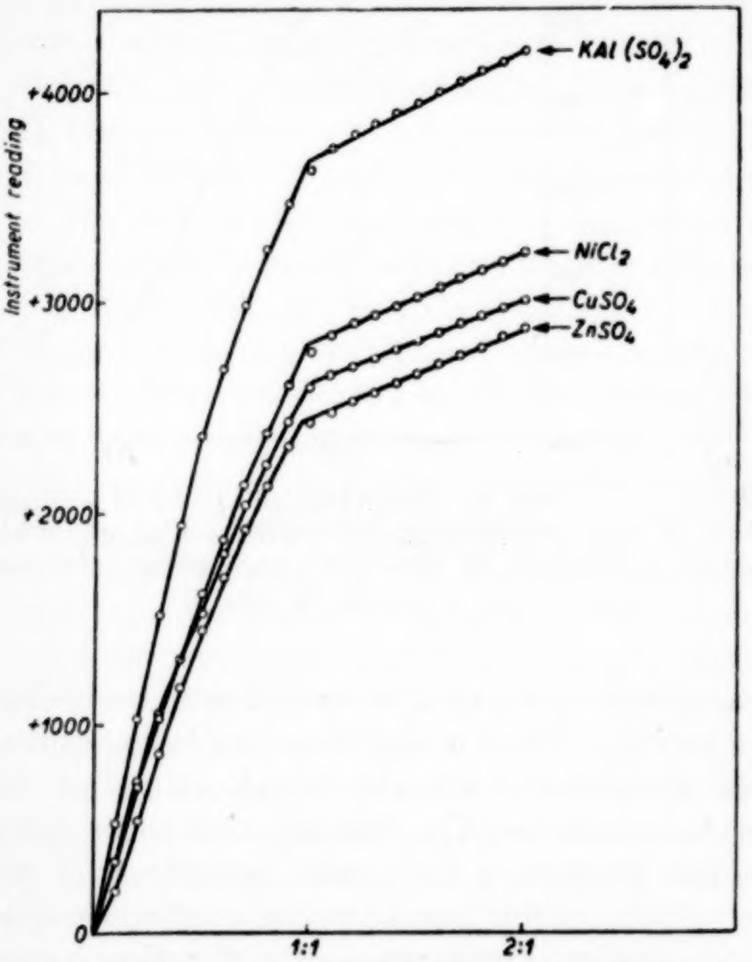

Fig. 6. Titrations of $1/3000 M$ ethylenediaminetetra-acetic acid with $1/150 M$ aluminum potassium sulfate, nickel chloride, copper sulfate and zinc sulfate.

DISCUSSION

Titration of ethylenediaminetetra-acetic acid with various bases yields curves having sharp reversal points at 2 mol equivalents of titrant. With barium and calcium hydroxides as the titrants, additional breaks are obtained at 4 mol equivalents of base. There is clear indication, therefore, that two hydrogens of the acid are readily ionizable, with the two additional protons dissociating so

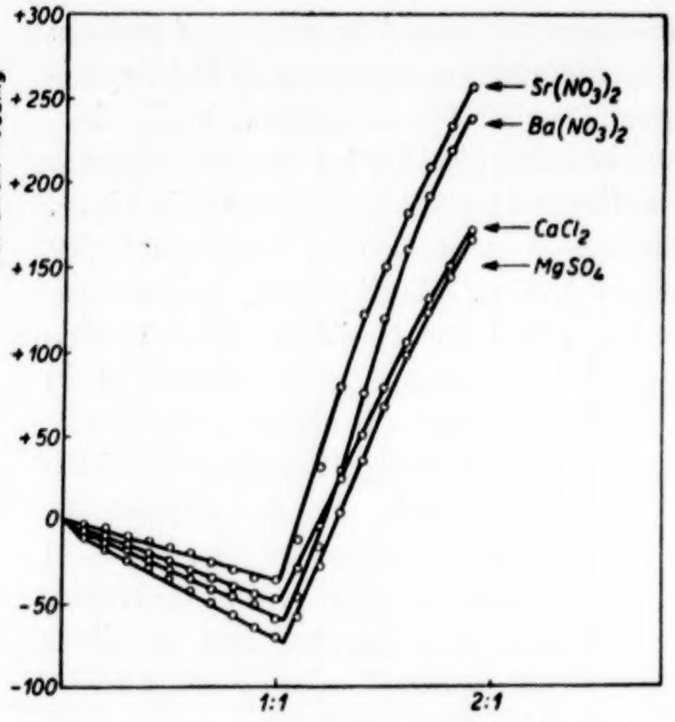

Fig. 7. Titrations of 1/1000M sodium ethylenediaminetetra-acetic acid with 1/50M alkali earth and magnesium salts at pH 10.

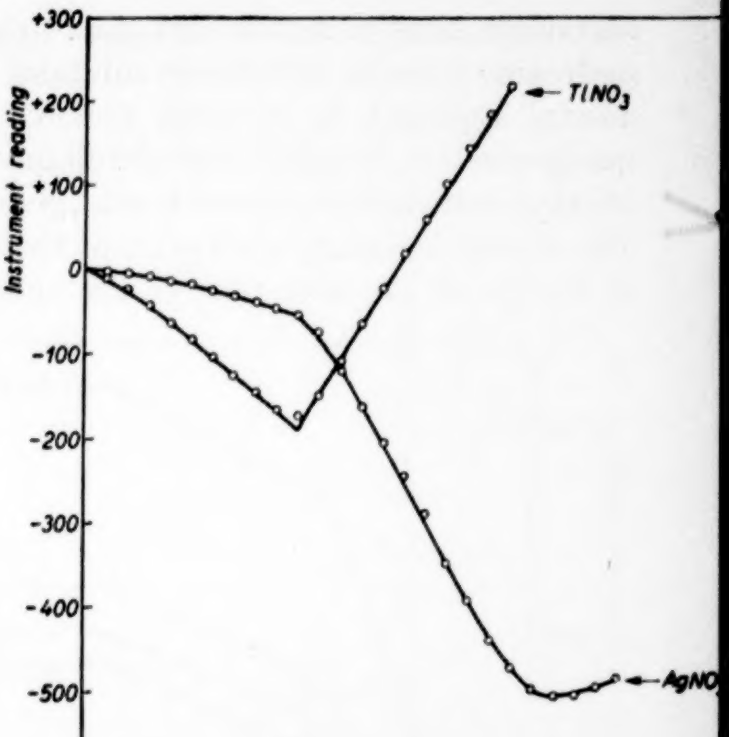

Fig. 8. Titrations of 1/1000M sodium ethylenediaminetetra-acetic acid with 1/50M thallous and silver nitrates at pH 10.

weakly that they are practically unavailable except under conditions of complexation whereby they have enhanced activity. These conclusions are in agreement with those of SCHWARZENBACH AND ACKERMANN[9] who list the pK values for the acid as 1.996(K_1), 2.672(K_2), 6.161(K_3) and 10.26(K_4). The titration curve using lithium hydroxide shows an inflection between 3 and 4 mol equivalents of the base. Potentiometric titration also discloses this break[5] giving confirmation of the reliability of the high frequency studies. Furthermore, the titration curves obtained with calcium and barium hydroxide in the present study are in agreement with those obtained by MARTELL[10] using conductometric titrations.

Titrations with sodium hydroxide of equimolar mixtures of ethylenediaminetetra-acetic acid and cobalt, nickel, copper(II), zinc, cadmium, manganese(II), lead, iron(III), or aluminum salts give curves having single inflection points at 4 mol equivalents of base. This indicates that the chelation of these salts is so strong that it takes place even at low pH and results in the displacement of all four salinogenic hydrogens of the acid. Similar titrations of the alkaline earth metals and magnesium yield curves having breaks at 2 and 4 mol equivalents of base, indicating that the first two hydrogens of the acid are ionized sufficiently to permit direct neutralization together with chelation with these metals. These metals do not form sufficiently strong complexes, however, to permit complete

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chelation at low pH and the titration curves show that after the first break at 2 mol equivalents, chelation plays an essential role in activating the remaining hydrogen ions. The case of calcium presents somewhat of an exception to this statement as shown by the slow first break in the calcium titration curve. The shape of the curve here indicates a moderately strong chelation, with the second two hydrogen ions being partially released by complexation at low pH.

Equimolar solutions of thallium(I) and silver with ethylenediaminetetra-acetic acid, when titrated with sodium hydroxide, show a simple acid-base neutralization curve with a break at 2 mol equivalents of titrant. After the initial break the titration curve rises rather steeply to a second break at 4 mol equivalents. Thallium (I) shows a tendency to complex principally at high pH as evidenced by the plateau formed between 3 and 4 mol equivalents of added base.

The various high frequency titrations described above give qualitative evidence that the chelating ability of metal ions falls in the following approximate order: Co, Ni, Cu(II), Zn, Cd, Pb, Fe(III), Al, Mn(II) > Ca > Mg, Sr, Ba > Ag, Tl (I) > Li > Na, K. This order is in good agreement with the formation constants for ethylenediaminetetra-acetic acid obtained by SCHWARZENBACH AND FREITAG[11], and agrees with the findings of MARTELL[10].

The results of the studies of reaction ratios as determined by acidity titrations of hydrogen ions liberated by continuous variation of the addendum in coexistence with metal ions, agree with the results described above. This technique is widely applicable for studying relatively instable complexes as well as those having high stability. Direct titration studies, which require that the complexation be sufficiently strong that stoichiometric reactions are assured, provide a rapid approach for establishing reacting ratios. Because of the stability restrictions, this method is highly dependent on pH control. In its favor, however, is the fact that the direct titration approach will give the absolute reacting ratios. This is in contrast to the hydrogen liberation techniques which show that the mol equivalents liberated reach a certain maximum value which in turn indicates a certain minimum ratio of reacting species. For example, ethylenediaminetetra-acetic acid may serve as a hexadentate addendum. If chelation occurs with a divalent metal the reaction product should have the general formula $H_2(M^{II}Y)$, and if a trivalent metal is involved, the reaction product should be, $H(M^{III}Y)$. In both cases, however, all four hydrogens of the original acid are titratable, either because of liberation or because of inhanced activity due to complexation.

Direct titration studies show the chemical composition of metal-ethylenediaminetetra-acetic acid complexes to be the product of reactions involving equal molar amounts of reactants. As a result of direct titration studies the approximate pH ranges for chelation can be suggested for the various metals studied: With the acid itself (pH about 2.5 to 3.0), Co, Ni, Cu(II), Cd, Pb, Mn(II), Fe(III) and Al chelate directly; with sodium ethylenediaminetetra-acetate at a pH of about 7, Mn(II) and Ca react; and with the sodium ethylenediaminetetra-acetate at pH 10, Mg, Ca, Ba, Sr, Ag, and Tl(I) react. These suggested ranges are in agreement with those previously suggested[12].

Thorium and rare earth elements show strong chelation tendencies with ethylenediaminetetra-acetic acid. Uranyl ion also reacts as disclosed by high frequency studies.

ACKNOWLEDGEMENT

The authors wish to express their appreciation to E. H. Sargent and Company for financial assistance during these studies. The cooperation of the Bersworth Chemical Company in supplying ethylenediaminetetra-acetic acid and its salts is also acknowledged.

SUMMARY

High frequency titrimetry is shown to be a versatile tool for studying complexation reactions. The formation, qualitative aspect of relative stabilities, and the chemical composition of various chelates of ethylenediaminetetra-acetic acid have been investigated by means of various high frequency techniques. The results obtained are in good agreement with results obtained by application of various other approaches.

RÉSUMÉ

Les titrations à haute fréquence permettent d'étudier les réactions de formation des complexes. La formation, le point de vue qualitatif des stabilités relatives et la composition de divers chelates de l'acide éthylènediaminotétraacétique ont été examinés par différentes techniques à haute fréquence. Les résultats correspondent bien à ceux obtenus par d'autres méthodes.

ZUSAMMENFASSUNG

Die Hochfrequenztitrationen ermöglichen eine Untersuchung der Bildungsreaktion von Komplexen. Der Bildungsvorgang, die entsprechenden Stabilitäten in qualitativer Hinsicht und die Zusammensetzung verschiedener Chelate der Ethylendiaminotetraessigsäure wurden mit Hilfe von verschiedenen Hochfrequenzmethoden untersucht. Die Resultate entsprechen denen, welche mit andern Methoden erhalten wurden.

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FORMIC ACID AS A REAGENT FOR ALKALINE PERMANGANATE

II. POTENTIOMETRIC DETERMINATION OF QUADRIVALENT SELENIUM

by

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In the permanganate methods for the determination of quadrivalent selenium, the oxidation is performed either in acid or alkaline media.

In the acid permanganate method[1], Se^{+4} is mixed with excess $KMnO_4$ together with sodium phosphate, and the excess of oxidant titrated after 10—30 min electrometrically with ferrous solution. In the alkaline method due to STAMM[2], oxidation with $KMnO_4$ is performed in 23—25% NaOH. After 10—15 min the solution is acidified, oxalic acid added together with Mn^{+2} ions and the excess of oxalic acid titrated with $KMnO_4$. This method necessitates the use of a blank as the alkalinity of the solution ($\sim 6N$ NaOH) is high enough to favour autodecomposition of $KMnO_4$[3].

According to TOMIČEK[4], direct oxidation of selenite with $KMnO_4$ in alkaline solution was unsuccessful, but approximate values were obtained by mixing the Se^{+4} solution with potassium permanganate in the presence of $\sim 0.7N$ NaOH, placing the mixture in boiling water for few minutes and titrating the excess of $KMnO_4$ with sodium arsenite. Although the reaction is carried out at a lower alkali concentration than in STAMM's method, heating favours autodecomposition of $KMnO_4$[5].

In the present investigation, recourse was taken to perform the oxidation of quadrivalent selenium with permanganate, directly in alkaline solutions, in view of finding out the best conditions under which a successful process can be performed. The reactions studied can be summarized in the following:

A) Oxidation of quadrivalent Se^{+4} with $KMnO_4$ in hot weakly or cold strong alkaline solutions.

B) Reduction of $KMnO_4$ with Se^{+4} in cold strong alkaline solutions, both in the presence and absence of Ba^{+2} ions.

C) Addition of Se^{+4} to $KMnO_4$ in strong alkaline solutions and then back-titrating the excess of the oxidant with formic acid[5].

The great difficulty encountered in the oxidation of selenite with permanganate is in disagreement with the magnitude of the equilibrium constant of the reaction K and its degree of completion α as calculated from the redox potentials of the systems involved[4] in the reactions:

i) in hot weakly alkaline solutions:

$$3\ \mathrm{Se}^{+4} + 2\ \mathrm{Mn}^{+7} \rightarrow 3\ \mathrm{Se}^{+6} + 2\ \mathrm{Mn}^{+4}$$

ii) in cold strong alkaline solutions:

$$\mathrm{Se}^{+4} + 2\ \mathrm{Mn}^{+7} \rightarrow \mathrm{Se}^{+6} + 2\ \mathrm{Mn}^{+6}$$

K for reaction (i) and (ii), can be calculated using previous relations[7] and taking E_0 for the systems $\mathrm{SeO_3}^{-2}/\mathrm{SeO_4}^{-2} = 0.03$, $\mathrm{MnO_4}^{-}/\mathrm{MnO_2} = 0.57$ and $\mathrm{MnO_4}^{-}/\mathrm{MnO_4}^{-2} = 0.54$ volts[6] thus:

(1) For reaction (i) in which the valency changes of the systems involved Z_1 and $Z_2 = 2$ and 3, the number of Faradays necessary to complete the reaction $n = 6$, K and α amount to $1.22 \cdot 10^{-55}$ and $1.1 \cdot 10^{-11}$ respectively.

(2) For reaction (ii) Z_1 and $Z_2 = 2$ and 1, $n = 2$, K and α amount to $5.15 \cdot 10^{-18}$ and $1.73 \cdot 10^{-6}$ respectively.

Both values of K and α indicate that the above reactions (i) and (ii) can take place quantitatively.

EXPERIMENTAL

The titration device and experimental procedure is similar to that previously described[7].

Preparation of solutions

a) $\mathrm{KMnO_4}$ solutions are prepared after the method of STAMM[8] and standardized with sodium oxalate[9] in acid solutions and with formic acid in alkaline ones[5].

b) Quadrivalent selenium solutions are prepared by dissolving sodium selenite grade Scherring Kahlbaum in twice distilled water. Its concentration was determined by the acid permanganate method[1]. The solutions so prepared and standardized possess normalities amounting to $0.1080N$ and $0.1053N$. Solutions of lower concentrations are prepared by appropriate dilution using boiled out twice distilled water. The solutions were checked now and then and proved to be stable over $\sim$ one month.

RESULTS

A) Oxidation of quadrivalent selenium with permanganate

In trying to force reduction of permanganate to $\mathrm{MnO_2}$, the reaction was primarily carried out in weakly alkaline solutions[10] ($\sim 0.1N$ NaOH). The reaction performed in the cold did not lead to quantitative results owing to the overlapping of the two processes:

(a) $\mathrm{MnO_4}^{-} \rightarrow \mathrm{MnO_4}^{-2}$ and

(b) $\mathrm{MnO_4}^{-} \rightarrow \mathrm{MnO_2}$

of which process (a) was the predominating one.

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To prevent reduction passing to MnO_2, the alkalinity of the selenite solution was then raised to 1—3N NaOH[10]. This reaction, which results in the quantitative reduction of MnO_4^- to MnO_4^{-2}, proceeds slowly, needing for the attainment of equilibrium ∿ 15 min for each 1 ml of the 0.1059N $KMnO_4$ at the beginning of the titration and ∿ 10 min for each 0.1 ml near the end-point. It could be accelerated with NaCl the concentration of which amounted to $10^0/_0$. Under these conditions, the reaction velocity was increased, such that only ∿ 6—8 min were needed for each ml of permanganate at the beginning and ∿ 5 min per 0.1 ml at the end-point. Several other catalysts such as ZnO, Zn^{+2}, Ag^+, Fe^{+3}, Cu^{+2}, Ni^{+2} and Co^{+2} ions were used but the equilibrium needed 12—13 min.

The titration curves

Curve C, Fig. 1 represents a titration performed in the cold and in the presence of 2N NaOH whereas curves A and B represent titrations performed in hot weakly alkaline solutions. In the presence of 2—2.5N NaOH an inflection amounting to ∿ 14—16 mv per 0.1 ml of $KMnO_4$ occurs at the end-point. This inflection although small is quite distinct as the change in potential before and after the end-point is much smaller. The inflection becomes less distinct at lower and higher alkalinities.

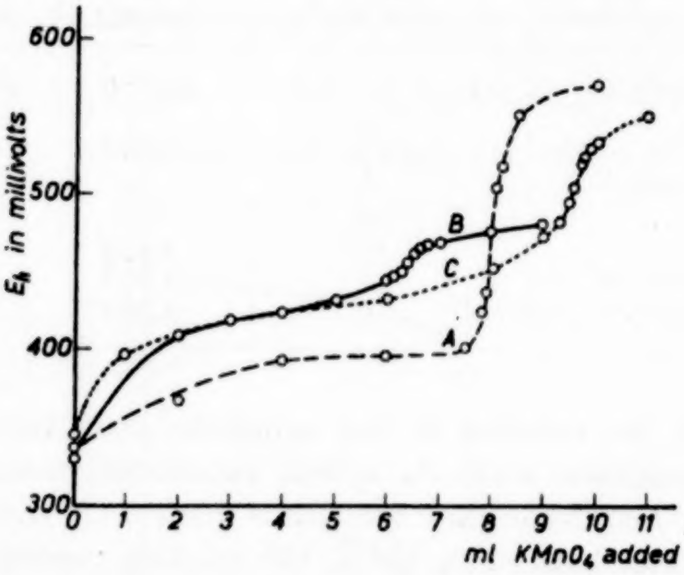

Fig. 1. (A) Titration of 5 ml 0.1053N Se^{+4} with 0.1097N $KMnO_4$ at 90° C
(B) Titration of 10 ml 0.00421N Se^{+4} with 0.01097N $KMnO_4$ at 90° C
(C) Titration of 10 ml 0.02106N Se^{+4} with 0.1097N $KMnO_4$ at 25° C

As may be seen from the data shown in Table I A results with errors not exceeding ∿ 0.33% are obtained when the alkali concentration is ∿ 1—3N NaOH and the amount of Se present 8 mg.

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TABLE I A

TITRATION OF 10 ml OF 0.02106*N* Se^{+4} WITH 0.1097*N* $KMnO_4$ AT 25° C

Alkali conc.	Max. inflec. per 0.1 ml $KMnO_4$	mg Se present	mg Se found	Error %
0.1*N*	7 mv	8.310 mg	8.209 mg	—1.21
1*N*	10 ,,	8.310 ,,	8.337 ,,	+0.33
2*N*	14 ,,	8.310 ,,	8.329 ,,	+0.23
2.5*N*	16 ,,	8.310 ,,	8.334 ,,	+0.29
3*N*	10 ,,	8.310 ,,	8.331 ,,	+0.25

TABLE I B

OXIDATION OF Se^{+4} WITH MnO_4^- IN 0.1*N* NaOH AT 90° C ($NaCl + AuCl_3$ catalyst)

Normality of $KMnO_4$	Normality of Se^{+4}		Max. inflec. per 0.1 ml $KMnO_4$	mg Se present	mg Se found	Error %
0.1097*N*	0.1053*N*	(5 ml)	37 mv	20.776	20.688	—0.37
,,	,,	,,	33 ,,	,,	20.646	—0.63
,,	,,	,,	15 ,,	8.310	8.258	—0.63
,,	0.02106*N*	,,	78 ,,	,,	8.284	—0.31
0.01097*N*	,,	,,	25 ,,	,,	8.336	—0.31
,,	,,	,,	17 ,,	4.155	4.134	—0.51
,,	0.01053*N*	,,	8 ,,	2.078	2.063	—0.72
,,	0.00421*N*	(10 ml)	6 ,,	1.662	1.659	—0.79

By carrying out the reaction in hot solutions, reduction of permanganate proceeds to the manganite state. As is well known this reaction is favoured at low alkalinities[10]. When the selenite solution is made 0.1*N* with respect to NaOH, and heated on a water bath to ∿ 90° C, the reaction needed ∿ 15 min for the attainment of equilibrium after each addition of titrant. By using NaCl as a catalyst, the reaction velocity increased so that only ∿ 8 min were required for equilibrium. Other catalytic agents were also applied including ZnO, Zn^{+2}, Ag^+, Fe^{+3} and Cu^{+2} ions, but the reaction velocity was only slightly increased, as it needed ∿ 12 min. Addition of 2—3 ml of a 0.5% auric chloride solution decreased the time of equilibrium to ∿ 10 min. The optimum catalytic agent used consists of a mixture of auric and sodium chloride, 2—3 ml of a 0.5% solution of the former + 2 g of the latter per 10 ml of selenite solution. In the presence of this mixture catalyst, the time of equilibrium reduced to ∿ 6 min.

The inflections at the end-points in the hot reaction are sharper than in the cold one, amounting in the case of the more concentrated selenite solution used (0.1053*N*) to 33—37 mv per 0.1 ml of permanganate, and decrease by declining selenite concentration. From Table I B it is apparent that with the more concentrated solutions used (0.1053—0.02106*N*) the errors vary from 0.3 to 0.6% but increase up to 0.79% in the most diluted solution (0.00421*N*) containing 1.662 mg Se per 10 ml of solution.

Reduction of permanganate with quadrivalent selenium

Reduction of permanganate by selenite in alkaline media leads to the production of manganate. Addition of selenite solution after the end-point leads only to a partial reduction of manganate to MnO_2. The reaction under these conditions proceeds more or less rapidly, needing ∿ 5 min at the beginning of the titration and ∿ 10 min at the end-point. The reaction velocity was not appreciably altered by the application of catalytic agents such as NaCl, HgO and ZnO.

The optimum alkali concentration favouring a quantitative reaction amounts to 0.5 — 3*N* NaOH. The errors amount in the case of the 0.1053*N* Se^{+4} solution to ∿0.21% but increase to 0.3—0.5% in the 0.0216*N* one.

At higher alkalinities than 3*N* NaOH and lower concentrations of the reacting solutions, erroneous results were obtained due to autodecomposition of $KMnO_4$ (*cf.* Table II A).

In weak alkaline solutions (∿ 0.1*N* NaOH), a very poor inflection occurs (*cf.* curve A, Fig. 2), which does not permit evaluation of the end-point. In 0.5*N*—3.5*N* NaOH (curve B, Fig. 2), the inflection increases to 25—40 mv in the case of 0.1053*N* Se^{+4} solution and 8—30 mv in the 0.0216*N* solution.

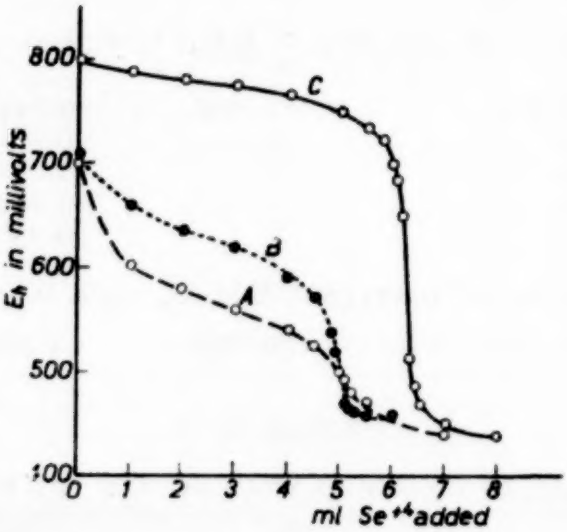

Fig. 2. Titration of 25 ml of 0.1059*N* $KMnO_4$ with 0.1053*N* Se^{+4}
(A) in 0.1*N* NaOH
(B) in 3*N* NaOH
(C) in 1*N* NaOH in presence of Ba^{+2} ions

By carrying out the titration in the presence of Ba^{+2} ions and keeping the alkali concentration at ∿ 1*N* (which alkalinity is the most suitable for quantitative reduction of $KMnO_4$ in the presence of Ba^{+2} ions[11]) considerable errors are observed which are attributed to the partial precipitation of $BaSeO_3$ that escapes oxidation resulting in a late end-point, although the titration curves (curve C, Fig. 2) are characterized by sharper inflections than in the absence of these ions. This is confirmed by the decrease of the error by decreasing the amount of Ba^{+2} ions added. In the more diluted solutions used, the end-point was attained early, but this can only be attributed to the autodecomposition of permanganate, catalyzed by the presence of Ba^{+2} ions[12] (*cf.* Table II B).

TABLE II A

REDUCTION OF $KMnO_4$ WITH Se^{+4} IN THE ABSENCE OF Ba^{+2} IONS

Alkali concn.	Max. inflec. per 0.1 ml $KMnO_4$	mg Se equivalent to $KMnO_4$	mg Se consumed	Error %
Titration of 25 ml 0.1059*N* $KMnO_4$ with 0.1053*N* Se^{+4}:				
0.1*N*	3 mv	20.901 mg	20.942 mg	+0.20
0.5*N*	25 ,,	,, ,,	,, ,,	+0.20
1.5*N*	38 ,,	,, ,,	,, ,,	+0.20
2*N*	35 ,,	,, ,,	,, ,,	+0.20
2.5*N*	34 ,,	,, ,,	20.859 ,,	—0.20
3*N*	33 ,,	,, ,,	20.652 ,,	—1.19
3.5*N*	39 ,,	,, ,,		
Titration of 10 ml of 0.1091*N* $KMnO_4$ with 0.0216*N* Se^{+4}:				
0.5*N*	8 mv	9.287 mg	9.244 mg	—0.46
0.8*N*	12 ,,	,, ,,	9.261 ,,	—0.29
1*N*	35 ,,	,, ,,	9.252 ,,	—0.38
1.5*N*	30 ,,	,, ,,	9.244 ,,	—0.46
2*N*	18 ,,	,, ,,	9.236 ,,	—0.55
Titration of 25 ml 0.02118*N* $KMnO_4$ with 0.01053*N* Se^{+4}:				
2*N*	15 mv	4.180 mg	4.267 mg	—2.09

TABLE II B

REDUCTION OF $KMnO_4$ IN 1*N* NaOH WITH Se^{+4} IN THE PRESENCE OF Ba^{+2} IONS

Max. inflec. per 0.1 ml $KMnO_4$	ml 5% $Ba(NO_3)_2$ soln	Se equivalent to $KMnO_4$	Se consumed in the titration	Error %
Titration of 25 ml 0.1059*N* $KMnO_4$ with 0.1053*N* Se^{+4}:				
140 mv	10	20.901 mg	25.930 mg	24.06
90 ,,	6	,, ,,	24.017 ,,	14.91
36 ,,	4	,, ,,	22.563 ,,	7.95
Titration of 25 ml 0.02118*N* $KMnO_4$ with 0.01053*N* Se^{+4}:				
68 mv	2	4.180 mg	4.139 mg	—0.99

C) *Oxidation of quadrivalent selenium with excess permanganate and back-titrating excess oxidant with formate*

TOMIČEK[4] applied this method for the determination of selenium using sodium arsenite as a reagent for back-titrating excess permanganate. This author accelerates the reaction by heating for some minutes on a water bath, a process which is always associated with considerable errors[5], resulting from the autodecomposition of permanganate. Furthermore, HEREDIA[13] prefers sodium formate over sodium arsenite in the back-titration of permanganate.

The method applied in this investigation consists in adding the selenite solution to potassium permanganate made 1*N* with respect to NaOH, measuring the potential of a bright platinum electrode immersed in the solution until it becomes constant indicating that equilibrium is attained. The time needed amounts on the average to ∿ 10—15 min. The excess of $KMnO_4$ is then titrated with a sodium formate or formic acid solution of the suitable concentration[5]. Good results were obtained for amounts of Se varying from 20—4 mg. When the amount of Se is 1.7 mg, the error becomes 0.57%. The errors become still higher (10%) when the Se present amounts to 0.5 mg, possibly due to the inability of the dilute selenite solution to react quantitatively with permanganate (*cf.* Table III).

TABLE III

Vol. and normality of $KMnO_4$	Normality of Se^{+4}	Normality formate	mg Se added	mg Se found	Error %
50 ml 0.1097*N* (no Ba^{+2} ions)	0.1053*N*	0.03825*N*	20.776 mg	20.832	+0.27
50 ml 0.1097*N* + Ba^{+2} ions *	,,	,,	,, ,,	20.874	+0.47
10 ml 0.1097*N* + Ba^{+2} ions *	0.02106*N*	0.0153*N*	4.155 ,,	4.143	—0.29
50 ml 0.01097*N* + Ba^{+2} ions *	0.00421*N*	0.00765*N*	1.162 ,,	1.653	+0.57
25 ml 0.01097*N* + Ba^{+2} ions *	0.00211*N*	,,	0.499 ,,	0.449	—10.0

* Ba^{+2} ions added in titrating excess $KMnO_4$ with formate

SUMMARY

Se^{+4} can be determined by mixing with $KMnO_4$ in 1*N* NaOH, stirring the mixture at room temperature and measuring the potential until equilibrium, which needs ∿ 10-15 min. Excess $KMnO_4$ is then determined with formate.

In the direct oxidation of Se^{+4} with MnO_4^-, in the cold, and in the presence of 2.5*N* NaOH and 10% NaCl, $MnO_4^- \rightarrow MnO_4^{-2}$. At 90°C, and in the presence of 0.1*N* NaOH, 10% NaCl and 2—3 ml of 0.5% $AuCl_3$, $MnO_4^- \rightarrow MnO_2$. The reaction which is rather slow is accelerated by the above reagents.

Reduction of MnO_4^- with Se^{+4} in 1—3*N* NaOH yields MnO_4^{-2}.

Like the indirect method, the direct potentiometric procedures yield good results.

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RÉSUMÉ

Se^{+4} peut être dosé par le permanganate en solution dans NaOH *N*. Ce mélange est agité à la température ordinaire; on mesure le potentiel jusqu'à l'équilibre (ce qui nécessite 10 - 15 min). L'excès de $KMnO_4$ est déterminé par un formiate.

Dans l'oxydation directe de Se^{+4} par MnO_4^- à froid, en présence de NaOH 2.5*N* et de NaCl à 10%, MnO_4^- est réduit en MnO_4^{-2}. A 90° C, en présence de NaOH 0.1*N*, de NaCl à 10% et de 2 — 3 ml de $AuCl_3$ à 0.5%, MnO_4^- est réduit en MnO_2. La réaction qui est plutôt lente est accélérée par les réactifs mentionnés ci-dessus.

La réduction de MnO_4^- par Se^{+4} dans NaOH 1—3*N* donne MnO_4^{-2}.

Comme pour la méthode indirecte, les procédés potentiométriques directs donnent de bons résultats.

ZUSAMMENFASSUNG

Se^{+4} kann quantitativ bestimmt werden mit Permanganat in normaler NaOH-Lösung. Dieses Gemisch wird bei gewöhnlicher Temperatur umgerührt. Man misst das Potential bis sich das Gleichgewicht einstellt (was etwa 10 bis 15 Min. benötigt). Der Überschuss an $KMnO_4$ wird mit einem Formiat bestimmt.

Bei der direkten Oxydation von Se^{+4} durch MnO_4^- ohne Erwärmen, in Gegenwart von NaOH 2.5*N* und 10% NaCl wird das MnO_4^- zu MnO_4^{-2} reduziert. Bei 90° C und in Gegenwart van 0.1*N* NaOH, 10% NaCl und 2 - 3 ml 0.5% iger $AuCl_3$-Losung, wird MnO_4^- in MnO_2 übergeführt. Die eher langsam verlaufende Reaktion wird durch die oben genannten Reaktive beschleunigt. Die Reduktion von MnO_4^- durch Se^{+4} in 1—3*N* NaOH gibt MnO_4^{-2}. Wie die indirekte Bestimmung, geben auch die direkten potentiometrischen Methoden gute Resultate.

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AUTOMATIC COULOMETRIC TITRATION OF ACIDS

by

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The general principles of coulometric titration with constant current, including applications to acidimetry and alkalimetry, have been reviewed by TUTUNDZIC[9] AND LINGANE[4]. Coulometric titrations are much easier to automatize than ordinary titrations with reagent solutions, and instruments for automatic coulometric titration have been described by several authors[1,3,5,7,10]. In a previous paper[5] the author demonstrated that the commercially available Beckman Model K Automatic Titrator (Beckman Instruments, Inc., South Pasadena, California), although designed for automatic potentiometric titrations with reagent solutions, can be adapted very easily to automatic coulometric titrations of the halide ions with electrolytically generated silver ion. The purpose of the present study was to determine the precision and accuracy of this apparatus when applied to the titration of hydrogen ion, using the glass electrode as indicator electrode and the platinum — silver/silver bromide generator electrode pair.

The combination of a platinum cathode and silver/silver bromide anode, which was used by LINGANE AND SMALL[6] as the basis of a titration coulometer and adapted to manual coulometric titrations of acids by CARSON AND KO[2], permits very simple cell design. The silver anode may be placed directly in the test solution, and the inconveniences and difficulties associated with diaphragm cells are avoided. SZEBELLEDY AND SOMOGYI[8] employed a silver/silver chloride anode in conjunction with a platinum cathode for coulometric titration of acids, but the silver/silver bromide anode is preferable because the concentration of dissolved silver(Ag^+ and $AgCl_2^-$ or $AgBr_2^-$) in equilibrium with it is much smaller. It is imperative that the concentration of dissolved silver be kept negligibly small, because its reduction at the platinum cathode would cause the current efficiency for the reaction $2H^+ + 2e = H_2$ to fall below the required 100%.

EXPERIMENTAL

The electrical instrumentation was the same as that used for the titration of the halides[5].

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The titration cell (Fig. 1) was a 70 ml weighing bottle provided with a machined plastic cover with holes for the various appurtenances. The platinum cathode and silver anode were both fabricated from stout wire coiled into flat helices and positioned horizontally one above the other and about 5 mm apart, near the bottom of the cell. The gross area of each electrode was 20 cm². A delivery tube was provided for passing carbon dioxide-free air through the solution to exclude atmospheric carbon dioxide. The ordinary glass electrode supplied with the Beckman autotitrator was used; it was positioned centrally in the cell just above the platinum cathode. The Beckman saturated calomel reference electrode was used, but since it is too large to fit conveniently in the cell it was placed in a small beaker of saturated potassium chloride solution and electrolytic connection to the test solution was completed by the usual type of inverted U-tube salt bridge containing saturated potassium chloride in 3% agar gel. The solution volume was 50 to 60 ml, and efficient stirring was provided by a magnetic stirrer.

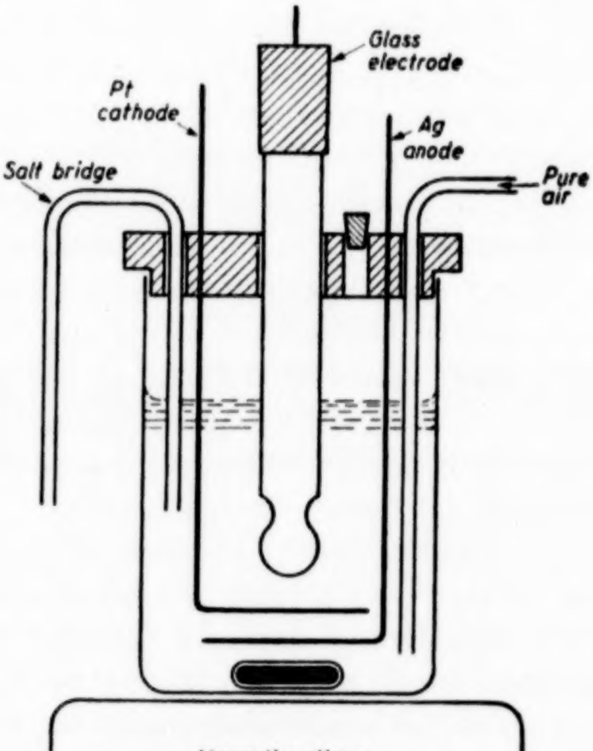

Fig. 1. Titration cell.

The electrolyte was 0.04M in respect to potassium bromide and 0.2 to 0.7M in respect to sodium sulfate which served to provide good conductance. The concentration of bromide ion should be large enough to insure that the potential of the silver anode will be maintained well below the value at which oxidation of water with concomitant production of hydrogen ion would occur, and yet must not be so large that a significant concentration of the soluble complex $AgBr_2^-$ is produced. The reduction of this complex to metallic silver at the platinum cathode would decrease the current efficiency for the reduction of hydrogen ion below the required 100%. The minimal bromide ion concentration depends on both the current density at the silver anode and the stirring efficiency. A concentration of about 0.04*M* proved to be ample with current densities up to about 5 milliamp/cm², and was small enough so that the solubility of silver bromide was negligible.

The silver anode may be used repeatedly before the silver bromide coating becomes so thick that it must be removed. No deleterious effect was observed with silver bromide coats corresponding to as much as 15 coulombs/cm²; *i.e.*, after about thirty successive titrations of 0.1 millimole samples at 20 milliamp with the particular cell and anode dimensions used. When necessary, the silver bromide coat may be removed by stripping in potassium cyanide solution, or when not excessively thick it may be reduced electrolytically by polarizing the silver electrode cathodically in hydrazine sulfate solution.

Precisely known quantities of hydrogen ion were obtained by weighing out samples of a dilute (*ca.* 0.012*M*) hydrochloric acid solution which had been prepared by weight from constant boiling hydrochloric acid.

The technique of the titrations was as follows. Forty ml of the supporting electrolyte (0.05*M* potassium bromide and 0.25*M* sodium sulfate) was placed in the cell, a small and unmeasured amount of hydrochloric acid (*e.g.*, 1 or 2 ml of *ca.* 0.01*M*) was added, and the autotitrator was set to pre-titrate the solution to the equivalence point pH, with a stream of purified air passing through the solution to exclude carbon dioxide. The sample of standard hydrochloric acid (10 to 12 g weighed to the nearest milligram) was then added from a weight buret, and the autotitrator was set to automatically titrate it. Several successive samples may be titrated without renewing the supporting electrolyte.

PERFORMANCE DATA

Fig. 2 shows the course of the observed titration curve in the immediate vicinity of the equivalence point, and the ideal theoretical curve for a strong acid — strong base titration.

The observed rate of change of pH at the equivalence point is somewhat smaller than the ideal curve for the titration of free hydrogen ion, because in the presence of the relatively large concentration of sulfate ion the added hydrogen ion exists predominantly as HSO_4^-, which is the actual species titrated. From the dissociation constant of HSO_4^- ($1 \cdot 2 \cdot 10^{-2}$) the ratio $(H^+)/(HSO_4^-)$ is equal to 0.06 when the sulfate ion concentration is 0.2*M*, so that about 94% of the added hydrogen ion is present as HSO_4^-. Doubtless the rate of pH change at the e.p. could be increased to more

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nearly the ideal value by using the sodium salt of a completly strong acid (*e.g.*, sodium perchlorate) as the supporting electrolyte. However, the slope of the observed curve in the sulfate solution at the e.p. is amply large (1.1 pH per second at 20 milliamp), and sodium sulfate is preferable to sodium perchlorate because it is more readily available commercially in the required degree of purity.

Table I summarizes the results obtained in automatic titrations of *ca.* 0.12 millimole samples of hydrochloric acid, corresponding to only *ca.* 1.2 ml of 0.1 M acid.

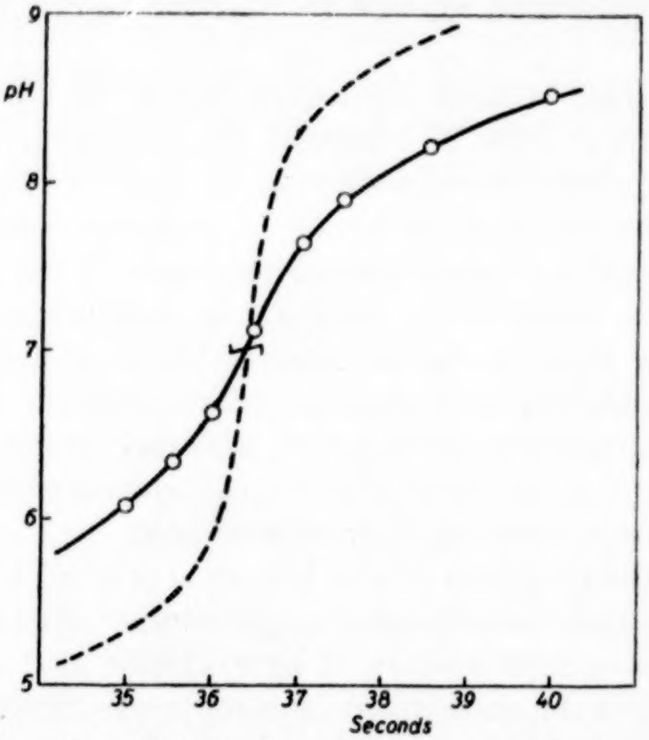

Fig. 2. Titration curve in vicinity of equivalence point of *ca.* $7.5 \cdot 10^{-3}$ millimoles of hydrochloric acid in 60 ml with generating current of 20 milliamp. The dashed curve is the theoretical curve for the titration of free hydrogen ion.

TABLE I

AUTOMATIC COULOMETRIC TITRATIONS OF HYDROCHLORIC ACID

HCl added Millimoles	Current Milliamp	Time Sec	pH Initial	pH Final	pH Diff.	HCl found Millimoles	Error %
0.12248	20.493	577.0	7.15	7.20	+0.05	0.12253	+0.04
0.13839	20.467	652.2	7.20	7.16	—0.04	0.13833	—0.04
0.11924	20.444	560.2	7.26	7.40	+0.14	0.11869	—0.46*a*
0.12811	20.382	606.7	7.14	7.25	+0.11	0.12815	+0.03*a*
0.13113	20.362	612.7	7.03	7.50	+0.47	0.13119	+0.05*a*
0.13618	20.336	645.3	7.50	7.46	—0.04	0.13599	—0.14*a*
0.14064	31.374	431.9	7.20	6.80	—0.40	0.14042	—0.16*b*
0.13687	31.374	419.8	6.80	6.80	0.00	0.13649	—0.28*b*
0.13527	20.434	639.9	7.26	7.40	+0.14	0.13551	+0.18*c*
0.13055	20.410	617.7	7.40	7.44	+0.04	0.13065	+0.08*c*
				Av.	±0.14	Mean	—0.07 ±0.15

a. $0.7M$ sodium sulfate instead of $0.2M$.
b. Autotitrator set at pH 6.60 instead of 6.80
c. Silver anode previously coated with silver bromide corresponding to 310 coulombs, or 15 coulombs/cm^2

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In most cases the autotitrator was set to stop at pH = 6.80, and the anticipation control was adjusted so that about 30 incremental applications of current occurred as the e.p. was approached. The exact "set point" is not critical, provided, of course, that the same setting is used in the pre-titrations and the actual titrations, and provided that it is not so far removed from the true e.p. that the precision is significantly decreased by the decreased slope of the titration curve.

As in the halide titrations these automatic titrations are subject to two small systematic errors; and end-point error, corresponding to the fact that the final pH inevitably differs slightly from the initial pH of the pre-titrated solution before the sample was added, and an "incremental error" resulting from a small net lag (*ca.* —0.008 sec) each time the electric stopclock operates. That both these effects are very small is shown by the fact that although no correction for them has been applied to the data in Table I the mean error is only —0.07% with an average deviation of ±0.15%. The smallness of the end point error is indicated by the small deviations between the initial and final pH values, which average ±0.14 unit and correspond to only ±0.1 sec at 20 milliamp. The negative incremental error is somewhat larger; when correction for it is applied the mean error is decreased to —0.02% but the average deviation from the mean (±0.14%) remains practically unchanged.

By using correspondingly smaller or larger generating currents, smaller or larger samples of hydrogen ion can, of course, be titrated.

It is evident that this same technique is generally applicable to many other acids, both strong and weak, and to acid mixtures. The only limitation is that the anion must not be reducible at the platinum cathode, and must not react in any way with the silver anode or with silver bromide (*e.g.*, by complexation).

SUMMARY

An apparatus is described for the automatic titration of acids by the constant current coulometric technique. The generator electrodes comprise a platinum cathode and a silver/silver bromide anode. The increase in pH resulting from the reduction of hydrogen ion at the cathode is indicated by a glass electrode, in conjunction with a Beckman Automatic Titrator which automatically monitors the titration and interrupts the generating current when the equivalence point pH is reached. Quantities of hydrochloric acid in the neighborhood of 0.12 millimole in 50 ml were titrated with a mean error of -0.07% and an average deviation from the mean of ±0.15%. The technique is applicable to any strong or weak acid, and to acid mixtures, provided that no substance is present which is either reducible at the platinum cathode or reactive in any way at the silver anode.

RÉSUMÉ

Un appareil est décrit pour le titrage automatique de l'ion hydrogène par la méthode coulométrique à courant constant. La cellule comprend une cathode de platine et une anode argent-bromure d'argent (avec Br^- en excès); les réactions sont: $2\ H^+ + 2e = H_2$ (cathode) et $Ag + Br^- = AgBr + e$ (anode). Le point d'équivalence est indiqué par une électrode de verre, et le titrage se complète automatiquement à l'aide d'un "Beckman Automatic Titrator". La quantité d'acide qui

a réagi est calculée (produit du temps mesuré (secondes) par le courant constant divisé par le nombre de faraday). On peut titrer l'acide chlorhydrique, en concentration de 0.12 millimole/50 ml environ, avec une erreur de 0.1% au maximum. Cette technique est applicable à tous les acides et mélanges d'acides, dont les anions ne se réduisent pas et ne réagissent pas avec l'argent.

ZUSAMMENFASSUNG

Ein Apparat wird beschrieben, der für die automatische Titration von Wasserstoffionen nach der coulometrischen Methode bei konstantem Strom anwendbar ist. Die Zelle besteht aus einer Platinkathode und einer Silberanode in einer Lösung welche einen Überschuss von Bromidionen enthält. Die Elektrodenvorgänge sind $2\ H^+ + 2e = H_2$ (Kathode) und $Ag + Br^- = AgBr + e$ (Anode). Der pH wird laufend von einer Glaselektrode kontrolliert, und die Titration unter Gebrauch eines Beckman Automatic Titrator am Aquivalenzpunkt automatisch eigenstellt. Chlorwasserstoffsaüre, in Mengen von *ca.* 0.12 millimol/50 ml, ist mit einem mittleren Fehler von weniger als 0.1% und einer mittleren Abweichung vom Mittelwert von *ca.* ±0.15% titrierbar. Das Verfahren sollte in der Bestimmung aller Säuren und Säuremischungen mit nichtreduzierbaren Anionen nützlich sein.

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POLAROGRAPHY OF NIOBIUM
I. REDUCTION IN MINERAL ACID MEDIA

by

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STROMBERG AND REINUS[1] studied the polarographic reduction of niobium in nitric acid solution and envisaged the following reactions at the dropping mercury cathode:

$$Nb^{+5} + 2e \rightarrow Nb^{+3} \dots\dots\dots\dots (1)$$
$$Nb^{+3} + 2H^{+} \rightarrow Nb^{+5} + H_2 \dots\dots\dots (2)$$

The reducible species in (1) was assumed to be the nitro-complex $[NbO(NO_3)_5]^{-2}$.

The present investigation relates to further studies with lower concentrations of niobium in nitric, hydrochloric, perchloric and sulphuric acids, which gives significant information on the general nature of the niobium complexes in these acidic media. It was also found necessary to modify some of the conditions laid down by STROMBERG AND REINUS.

EXPERIMENTAL

Niobium pentoxide (Johnson & Matthey) was fused with potassium carbonate in a platinum crucible and made into a stock solution in water, the niobium content of which was determined gravimetrically. The reagents used were of A.R. grade. Their solutions, and the solution of gelatine (commercial), which was prepared freshly before each experiment, were all tested separately and found to be polarographically blank in the range of our study. The polarograms were recorded in a Tinsley (Type 12) automatic pen-recording polarograph at 28.5 ± 0.2° C, using a cell with an internal mercury pool anode. The solutions were deoxygenated by bubbling purified nitrogen for about 15 minutes before each recording, and stabilized by adding gelatine (0.005% w/v) after acidification. The results, observed in the range of —0.5 V to —1.5 V with damping set at 2, are given in Fig. 1-8 and in Table I. The half-wave potentials are not corrected for the anode potentials, and for the resistance of the solutions under different conditions.

RESULTS AND DISCUSSION

TABLE I

HALF-WAVE POTENTIALS AGAINST INTERNAL MERCURY POOL ANODE

	Acid (M)	External electrolyte added (M)	Niobium (mM)	$E_{\frac{1}{2}}$ (Volt)
1	HNO_3 (0.12)	Nil	0.0235	—1.2
2	do. (0.15)	KNO_3 (0.4)	do.	—1.18
3	do. (0.02)	KNO_3 (0.6)	0.035	—1.25
4	do. (0.15)	KCl (0.8)	0.0235	—0.88
5	HCl (0.16)	KNO_3 (1.0)	do.	—0.89
6	$HClO_4$ (0.14)	$NaNO_3$ (0.48)	do.	—1.175

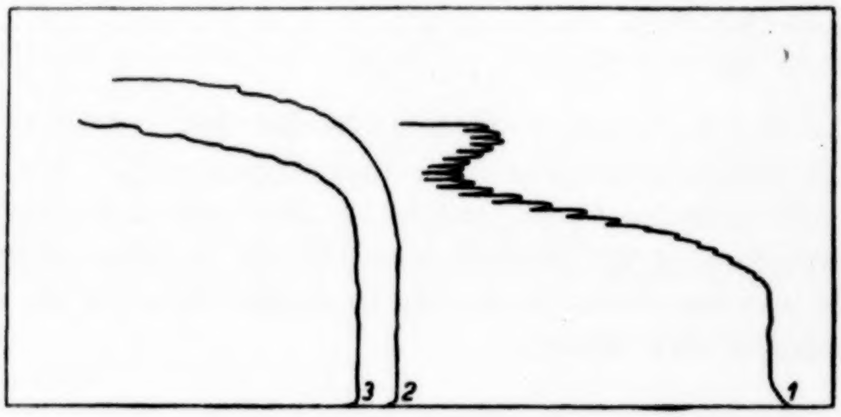

Fig. 1

Curve 1 : Nb 0.047 mM, HNO_3 0.12M, *Sn* 100
Curve 2 : Nb nil, HNO_3 0.15M, *Sn* 100
Curve 3 : Nb nil, HNO_3 0.15M, KNO_3 1.0M, *Sn* 100.
Sn (sensitivity) denotes total microamperes per full scale.

Curve 1, Fig. 1, shows a typical niobium reduction wave having a well-formed hump preceding final discharge of the hydrogen ion. This resembles in form that of a catalytic reduction wave of the perrhenate ion in a buffer medium[2]. The hump formation could not be suppressed by increasing the concentration of gelatine even fourfold. As we have shown, the shape of this hump could be changed under certain conditions, but the upper level of the peak remained unaffected. Hence the wave heights were always measured from the peaks, as indicated in Fig. 8.

Factors influencing the main hydrogen overpotential

(a) *Ratio of* $[H^+]$ *to* $[Nb^{+5}]$: Fig. 2 (curves 1-3) shows that the resolution of the catalytic niobium reduction wave from the main hydrogen discharge wave depends critically upon the main hydrogen over-potential, which, in turn, is dependent on the ratio of $[H^+]$ to $[Nb^{+5}]$. It was also observed that, below a concentration of *ca.* 0.005 m*M* of niobium, no satisfactory resolution of the two could be obtained at any concentration of HNO_3.

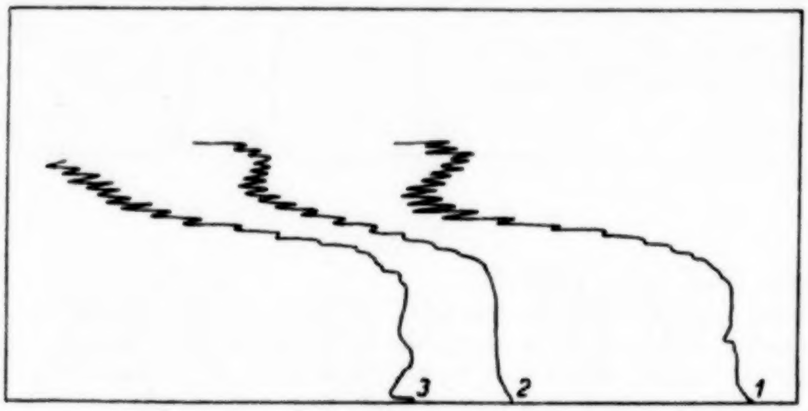

Fig. 2

Effect of the ratio (H^+) : (Nb^{+5}) on main hydrogen over-potential
Curve 1 : Nb 0.035 m*M*, HNO_3 0.225*M*, *Sn* 100
Curve 2 : Nb 0.012 m*M*, HNO_3 do. *Sn* 50
Curve 3 : Nb 0.007 m*M*, HNO_3 do. *Sn* 20.
Sn (sensitivity) denotes total microamperes per full scale.

(b) *Ratio of* $[KNO_3]$ *to* $[Nb^{+5}]$:

Fig. 3 (curves 1-2) shows that the main hydrogen discharge potential decreases with an increase in this ratio in the same way as $[H^+]$: $[Nb^{+5}]$. The resolution is improved by increasing the proportion of niobium (curve 3). Curves 2 and 3 in Fig. 1 show that the hydrogen discharge potential in a pure nitric acid solution is also lowered by the addition of KNO_3.

Formation of niobium complexes in acid media

Recently, ELSON[3] reported to have obtained a reduction wave of niobium at $E\frac{1}{2} = -1.26$ V (S.C.E.) in a 0.1*N* chloride medium at pH 2.6. Our experiments with more acidic solutions resulted in H-discharge before the above potential could be reached. STROMBERG AND REINUS had also failed to obtain the niobium reduction wave in hydrochloric acid solutions, apparently for the same reason. ELSON did not indicate the nature of the reducible species in his communication.

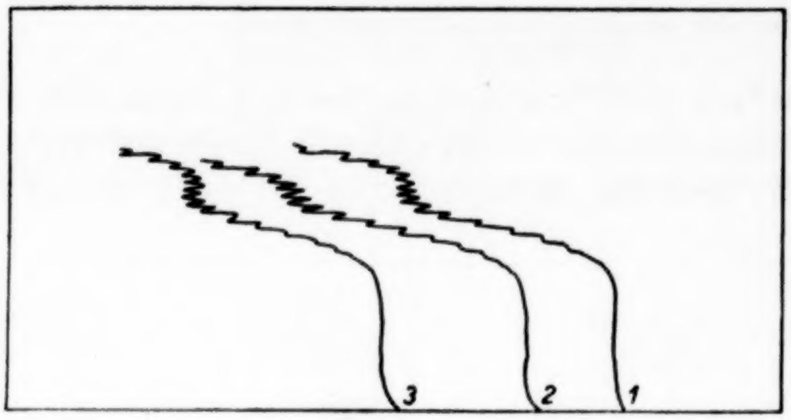

Fig. 3

Effect of the ratio (KNO_3) : (Nb^{+5})
Curve 1 : Nb 0.012 mM, HNO_3 0.15M, KNO_3 0.6M, *Sn* 50
Curve 2 : Nb 0.012 mM, HNO_3 0.15M, KNO_3 1.0M, *Sn* 50
Curve 3 : Nb 0.021 mM, HNO_3 0.15M, KNO_3 1.0M, *Sn* 100.
Sn (sensitivity) denotes total microamperes per full scale.

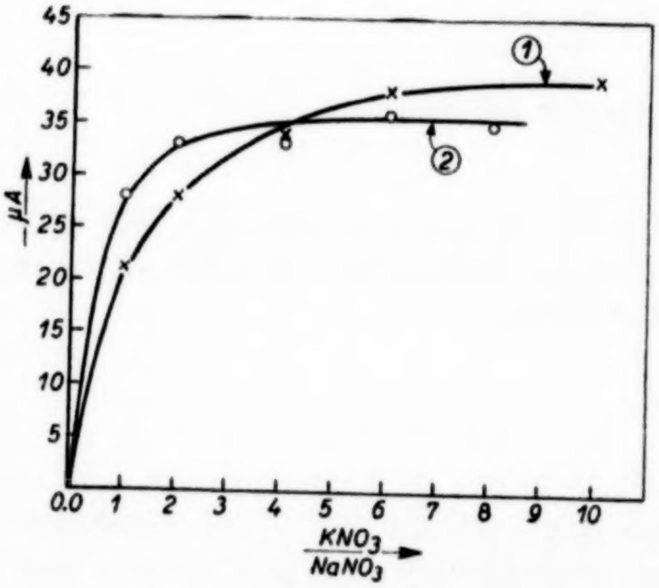

Fig. 4

Effect of NO_3^- ion on solutions of niobium in HCl and $HClO_4$
1 Unit KNO_3 = 0.1M, 1 Unit $NaNO_3$ = 0.12M
Curve 1 : Nb 0.0235 mM, HCl 0.16M, KNO_3 0—1M
Curve 2 : Nb 0.0235 mM, $HClO'$ 0.14M, $NaNO_3$ 0—0.96M.

As discussed later, the niobium in such solutions is likely to be present as a mixture of the chloro- and hydroxy-complexes. Since we did not observe any reduction wave due to the hydroxy-complex (Fig. 6, curves 1 and 2) it appears to us that the reducible species in ELSON's study was the chloro-complex of niobic acid.

Our attempts to get reduction waves due to niobium in perchloric and sulphuric acid solutions gave negative results. But by adding alkali nitrate, well-defined waves appeared in hydrochloric and perchloric acid solutions (Fig. 4, curves 1 and 2), but only a small and transient wave was indicated in a 0.015M H_2SO_4 solution of 0.0235 mM niobium. Also in the media of nitric acid of low concentrations, the addition of KNO_3 increased the waveheights (Fig. 6, curves 1 and 2). Conversely, the addition of KCl or $KClO_4$ to a niobium solution in nitric acid progressively decreased the height of the waves due to niobium (Fig. 5, curves 1 and 2), contrary

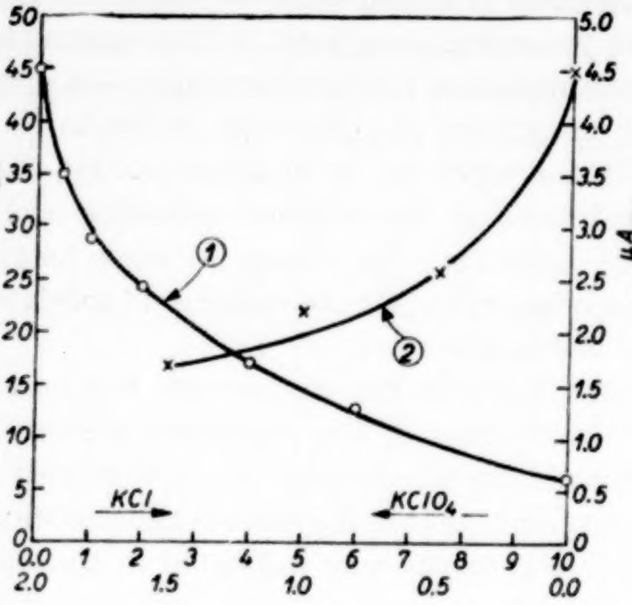

Fig. 5

Effect of Cl^- and ClO_4^- ions on solutions of Nb in HNO_3

1 Unit KCl = 0.1*M*, 1 Unit $KClO_4$ = 0.072*M*

Curve 1 : Nb 0.0235 m*M*, HNO_3 0.15 *M*, KCl 0—1.0 *M*

Curve 2 : Nb 0.0235 m*M*, HNO_3 0.03*M*, $KClO_4$ 0—0.108 *M*.

to what happens when potassium nitrate is added (Fig. 6 curves 1 and 2). These observations can be explained by assuming the following mass action equilibrium:

$$[\mathrm{NbO}\ (\mathrm{NO_3})_5]^{-2} + 5\ \mathrm{x}^- \rightleftharpoons [\mathrm{NbO}\ \mathrm{x}_5]^{-2} + 5(\mathrm{NO_3})^-$$

$$K = \frac{[(\mathrm{NbO}\ \mathrm{x}_5)^{-2}]\ [(\mathrm{NO_3})^-]^5}{[(\mathrm{NbO(NO_3)_5})^{-2}]\ [\mathrm{x}^-]^5}$$

where X = OH, Cl, ClO_4 or $\frac{1}{2}(SO_4)$.

In our studies, the waves are assumed to be due to the reduction of the nitroniobate complex, and their heights are proportional to its concentration. The

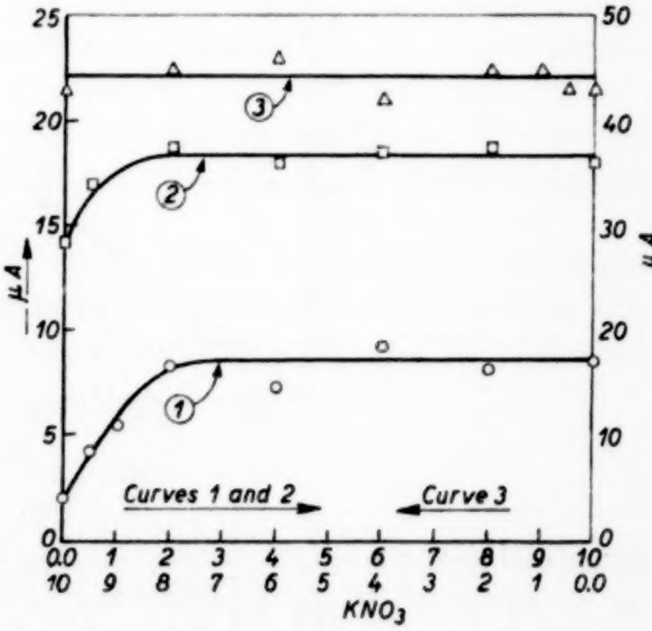

Fig. 6

Effect of acidity on the stability of the nitro-complex

1 Unit KNO_3 = 0.1*M*

Curve 1 : Nb 0.035 m*M*, HNO_3 0.02*M*, KNO_3 0—1*M*

Curve 2 : Nb 0.012 m*M*, HNO_3 0.075*M*, KNO_3 0—1*M*

Curve 3 : Nb 0.021 m*M*, HNO_3 0.15*M*, KNO_3 0—1*M*.

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small and transitory nature of the limiting current in sulphuric acid medium containing potassium nitrate, reported in the preceding paragraph, indicates that the sulphate ion forms a strong complex with niobium, irreducible under the given conditions. For the same reason, small quantities of potassium sulphate (0.03 molar) were found to suppress completely the wave due to niobium (0.0235 mM) in 0.15M nitric acid. A quantitative estimate of the relative affinities of the complexing anions should be possible by measuring the change in wave heights caused by the proportional addition of the complexing ions to niobic acid solutions, and will be attempted in a subsequent communication.

The halogen complex, $(NbOCl_5)^{-2}$ is mentioned in the literature[4]. The corresponding nitro-, perchloro- and sulphato-complexes in the respective acid media may be assumed by analogy. The hydrolysis of the nitro-complex at lower acidities (Fig. 6 curves 1 and 2)should also follow parallelly that of the chloro- and perchloro-complexes, which have comparable stabilities, in the way indicated in the mass action equation above.

Proportionality of limiting current to niobium concentration

Fig. 7 shows the direct proportionality between the limiting current and the concentration of niobium in nitric acid of strength 0.12M. STROMBERG AND REINUS recommended the addition of KNO_3 in the niobium solutions for getting well-defined waves. Our observation is that such additions have only a levelling effect on a hump preceding the main hydrogen discharge without affecting the peak

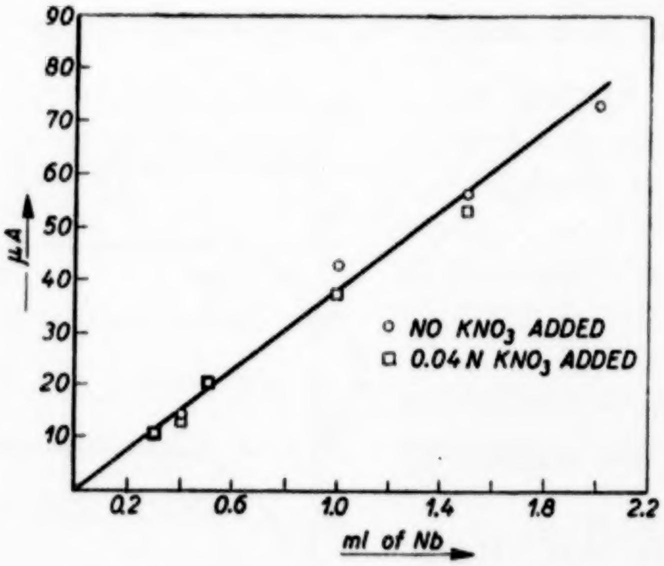

Fig. 7

Concentration-wave height proportionality curve (with residual current correction).
(1 ml Nb = 0.0235 mM)
Nb 0.3 ml — 2.0 ml, HNO_3 0.12M

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value of the wave, and would thus appear to be redundant, in the medium of nitric acid of sufficient concentration.

By increasing the height of the mercury column to give drop-time values varying from 3.3 secs to 1.7 secs, the limiting current decreased by about 5% (Fig. 8, curves 1-3). The reason for this apparent departure from the general criterion of a catalytic reduction wave[5] may be the unusual reaction mechanism in this case involving adsorption on the dropping mercury surface prior to the reaction[1]

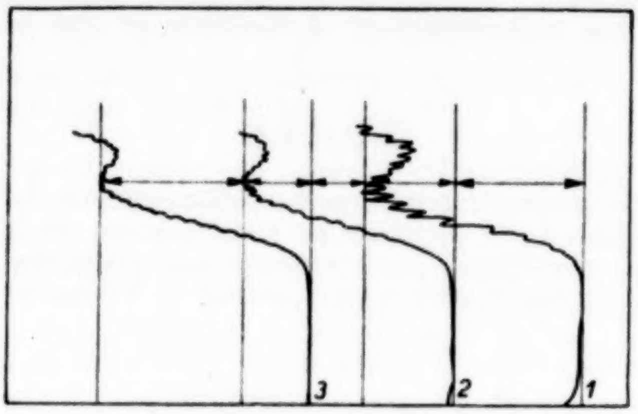

Fig. 8.

Effect of the mercury column height on limiting current.
Nb 0.0235 m*M*, HNO_3 0.15*M*, *Sn* 100
Curve 1 : Drop time 3.3 sec
Curve 2 : do. 2.2 sec
Curve 3 : do. 1.7 sec
Sn (sensitivity) denotes total microamperes per full scale.

The limiting current values observed by us are relatively much higher than those reported by STROMBERG AND REINUS[1]. For example, their values for 0.9 m*M* Nb in 0.2*M* HNO_3 solution containing 0.0035% gelatine is about the same as observed by us for 0.037 m*M* Nb in 0.12*M* HNO_3 solution containing 0.005% gelatine (Fig. 7). Low values may be caused by the partial precipitation of niobium in the absence of a requisite amount of gelatine. On the other hand, excess of gelatine should also reduce the limiting current by adsorption on the dropping electrode surface[1]. The complexity of the phenomenon does not admit of a further discussion at this stage.

Experiments using the S.C.E. anode cell, to study the relative stabilities of the niobium complexes and the mechanism of reduction of niobium in other complexing media, are in progress, and will form the subject of a future communication.

ACKNOWLEDGMENT

The author thanks Dr. A. B. BISWAS for his valuable advice, suggestions and helpful criticism throughout the investigation, and Dr. J. GUPTA for his encouragement and guidance. He also records his appreciation to Mr. M. Y. LELE for help in instrumentation.

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SUMMARY

The formation and interconversion of the nitro-, chloro-, perchloro- and sulphato-complexes of niobium in mineral acid media and the reduction of the nitro-complex have been studied. Conditions for a linear proportionality between the limiting current and the concentration of niobium in the microgram range have been worked out.

RÉSUMÉ

L'auteur a étudié la formation et les transformations des nitro-, chloro-, perchloro-, et sulfatocomplexes du niobium en milieu acide, et également la réduction du nitrocomplexe. Les conditions pour obtenir une proportionnalité linéaire entre le courant limite et la concentration en niobium (à l'échelle micro) ont été mises au point.

ZUSAMMENFASSUNG

Es wird über die Bildung und gegenseitige Umwandlung des Nitro-, Chloro-, Perchloro- und Sulphato-komplexes des Niobiums in mineralsaurem Medium und über die Reduktion des Nitrokomplexes berichtet. Die Bedingungen für eine lineare Beziehung zwischen Grenzstrom und Konzentration des Niobiums im Mikrogrammgebiet sind festgelegt worden.

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BOOK REVIEWS

Analisi cromatografica su carta, by GIUSEPPE SCHOEN. Soc. Edit. Farmaceutica, Milano, 1954, 352 pages, 296 tables. Price L. 3000.

Amongst the number of books on paper chromatography that have appeared in the last few years, this one is distinctive in that it attaches the greatest importance to a detailed survey in the text, tables and diagrammatic drawings of the properties of the compounds investigated by paper chromatography. Thus it supplements excellently the other books on this subject. The fact that it is written in Italian should not prevent those not familiar with Italian from finding the book useful, as the tables and diagrams, which comprise the majority of the book, can be understood by all.

The compounds are divided into a number of groups: amino acids, amines, peptides, purines etc, vitamins, organic acids, alkaloids, carbohydrates, alcohols, sulphonamides, antibiotics, sterines and steroids, enzymes and inorganic compounds. After an introduction there follows a table for each compound, which gives the found R_F values and information on the experimental conditions. Then follows a number of diagrams which show, for each group of compounds, the R_F values determined by the use of the various solvents.

This excellent survey would have been even better if the author had brought the literature up-to-date immediately before publication, and if he had made a greater effort to give as complete a survey of the literature as possible. A Scandinavian reviewer cannot help but notice the absence of any mention of several Scandinavian papers, *e.g.* of Finnish work on sulphonamides and Norwegian work on analgesics and antipyretics.

F. REIMERS (Copenhagen)

Fluorescence Analysis in Ultra-Violet Light, by J. A. RADLEY AND JULIUS GRANT. Fourth Edition, revised. Chapman & Hall Ltd., London 1954, 560 pages, 45 illustrations. Price 52*s*.6*d*. net.

RADLEY AND GRANT's well-known textbook, which was published in three editions within the space of few years before the war and then re-printed twice, has now appeared in a new edition, which is brought up-to-date with regard to literature from the war years and subsequent years. The extent to which the book has been revised is shown by the fact that the number of papers which are mentioned has increased by about 50%.

However, the arrangement of the book is unaltered. It is introduced by short chapters on theory, apparatus and methods. The following 20 chapters comprise a thorough survey of the literature and the authors' own experiences concerning fluorescence analysis in all its forms: the observation of fluorescent light, quantitative fluorometric determinations, fluorescence microscopy, titration with fluorescence indicators, etc. The survey includes organic and inorganic chemistry, medicine, bacteriology, botany, many spheres of the technical analysis, *e.g.* of glass, metals, drugs, foodstuffs, oils, leather, minerals, dyes, paper, gums and textiles, as well as criminological and museum work. All these chapters are carefully revised and in many cases considerably extended.

This new edition of the book will, to a still greater extent, be of benefit to all who wish to become acquainted with the numerous experiments on fluorescence analysis.

F. REIMERS (Copenhagen)

Organic Coating Technology, Volume I, par H. F. PAYNE. John Wiley, New York; Chapman & Hall, Londres, 1954, 674 pp., 96 fig., 216 tableaux et formules, Bibliographie, Prix: $ 10.00.

L'auteur, Mr. H. F. PAYNE, professeur au Polytechnic Institute de Brooklyn, Technical Editor de la firme: American Cyanid Co. est un spécialiste bien connu dans le domaine des Peintures, Vernis et Plastiques, en particulier par sa coupe de perméabilité, et par l'appareil d'essai par immersion: Dip Coater de Fischer-Payne.

L'ouvrage qui comprendra deux volumes, dont le premier est seul paru à cette date, s'adresse avant tout aux personnes qui doivent se mettre au courant de l'industrie des peintures et de leurs matières premières. En fait, sa valeur documentaire dépasse de beaucoup ce cadre, et il sera consulté et étudié avec fruit par les spécialistes de la profession.

Les deux volumes formeront un tout, englobant la théorie et la pratique de l'industrie des peintures, vernis et matières filmogènes.

Le tome I contient l'exposé des matières premières pour l'industrie des peintures et vernis; le tome II devra traiter des pigments, de la fabrication et des applications des peintures et vernis.

A un premier chapitre de généralités: liaisons chimiques, polarités, formation du film, font suite quatorze chapitres traitant des matières premières: huiles et préparations dérivées (standolies, huiles soufflées, condensation des acides gras à la pentaérythrite, huiles copolymérisées au styrolène, etc . . .); étude de la siccativité et de la polymérisation. Résines naturelles, Phenoplastes et résines synthétiques. Vernis, siccatifs, solvants, résines alkydes, aminoplastes, élastomères, plastifiants, dérivés cellulosiques. Résines vinyliques et acryliques, silicones, esters du titane.

Enfin, un dernier chapitre, qui intéressera l'analyste, a trait aux méthodes d'essai physico-chimiques; il s'agit, par exemple, des déterminations suivantes: viscosité, densité, solubilités, indices de réfraction, absorption dans l'UV, tests de gélification, d'applicabilité, mesure des épaisseurs, de la flexibilité, de la perméabilité, de la résistance électrique, des indices chimiques (indices d'acide, d'iode, de saponification, d'acétyle, indice diénique, etc . . .).

L'ouvrage, d'une présentation parfaite, est de plus agrémenté, en tête des chapitres, de citations philosophiques, scientifiques, morales, d'une grande hauteur de pensée.

M. JEAN (Paris)

Bilder zur qualitativen Mikroanalyse anorganischer Stoffe von WILHELM GEILMANN, Universität Mainz, unter Mitwirkung von WALTRAUD GEILMANN, zweite erweiterte Auflage. Verlag Chemie, G.m.b.H., Weinheim/Bergstr., 1954. 120 S., 393 Abb. auf 50 Taf. Ganzl. DM 20,80.

This second edition of GEILMANN's well-known book is quite a valuable asset to qualitative microanalysis. The first edition of 1934 gave only 240 photos, this one nearly 400. Moreover the indications for carrying out the reactions have been considerably improved and extended, so that by now the book may be said to be an excellent manual of microscopic identification reactions.

From its very nature the choice of reactions is rather arbitrary. That is an advantage. As the number of known microscopic reactions is far greater than those treated here, a judicious selection, made by an expert as the author evidently is, must always be appreciated. The lay-out of the book, and particularly the photographic part of it, are excellent and explain its rather high price. Altogether we must be very glad that the author took the trouble to bring his book well abreast of the times.

And yet one is inclined to give utterance to some criticism or at least to raise some questions. So in the first place, why did not the author write a complete text-book on microscopic analysis? It is clear that the final identification of the ions is only half the work, and as often as not, the easiest part of it. All the previous technique, bringing into solution, separating from interfering ions etc., is at least as important and quite often decisive for the choice of the identification reaction.

When the author gives a number of ractions for the same element, why does not he indicate which one is in his opinion the most recommendable under the given conditions?

In the title the word "microanalysis" is used, whereas "microscopic analysis" is meant. There is already so much confusion in this respect, so why make it worse? There seems to be no reason at all to claim the prefix micro for microscopic reactions only.

Finally it is to be regretted that in the bibliography at the end of the preface the name of J. GILLIS as a joint-author has been left out when the Union Report is mentioned. Let us presume that it happened unintentionally.

C. J. VAN NIEUWENBURG (Delft)

Thermo-Mikro-Methoden zur Kennzeichnung organischer Stoffe und Stoffgemische, von LUDWIG KOFLER UND ADELHEID KOFLER, unter Mitarbeit von MARIA BRANDSTÄTTER, dritte erweiterte Auflage. Verlag Chemie, G. m. b. H., Weinheim/Bergstr., 1954. 608 Seiten, 247 Abb., 16 Taf. Ganzl. DM 39,80.

The work of L. KOFLER, deceased, and his co-workers on the use of micro-techniques for the identification of organic substances, especially by means of the hot-table microscope, is too well known to require much discussion. The fact that the two first editions of his book were out of print in six years time is ample proof of its usefulness, so that it is hardly necessary to enlarge upon its particular features and merits. This third edition reviews a great many improvements which have been brought about in the Innsbruck laboratory in the course of the last years, and moreover brings some new chapters, among others about the use of the polarization microscope for identification purposes.

Of course it is all very much "KOFLER"; everything is done by means of his own special apparatus and his own special methods. One might differ in opinion whether these are the only good ones, but one could not deny that together they form an excellent and coherent set of procedures, covering a wide field of organic analysis.

The identification tables, occupying nearly one half of the book, have been quite considerably increased since the second edition. Arranged according to increasing melting points, they provide data on the eutectic melting points with a set of standard compounds and on the refractive indices of over 1000 organic substances, with a marked but not exaggerated preference for products of pharmaceutical interest.

The lay-out of the book is excellent, and considering the vast amount of work which must have been done for its accomplishment, the price is not excessively high.

C. J. VAN NIEUWENBURG (Delft)

A French-English Dictionary for Chemists, by A. M. PATTERSON. Second edition. John Wiley & Sons, Inc., New York, Chapman & Hall, Ltd., London, 1954, xiv + 476 pages. $ 6.50.

The first edition was published in 1921, with a vocabulary of 35,000. This has now grown to 42,000, in spite of the fact that many terms having the same meaning and spelling in French and English have been omitted in order to save space.

More than 17 technical vocabularies were consulted for the 2nd edition, in the fields of chemistry, physics, mechanics, medicine, biology, geology, technology of petrol and of aviation.

Some idea of the scope of the dictionary may be given by a few quotations from the Introduction: a large number of phrases has been included; labels such as *Anat.*, *Elec.* and *Soap* are freely used to indicate in what connection a word has a given meaning; irregular verb forms which are likely to appear in scientific literature are given where they are most needed, *i.e.* under their own spellings, and not concealed under the parent verb. The Introduction also gives useful notes on feminine and plural forms (which are not given in the vocabulary except in special cases), on nouns used as adjectives, and inorganic and organic nomenclature. The English version should be in accord with the usage of the American Chemical Society "Directions to Abstractors"; *e.g. oxy-* is translated by *hydroxyl-* when it designates hydroxyl, but by *oxo-* or *keto-* when it designates the ketonic group. Many other differences between French and English chemical nomenclature are usefully summarized.

The book is very well produced, with clear print on good quality paper and a pleasing semi-flexible binding.

The first edition of this book, and also PATTERSON's *German-English Dictionary for Chemists* have, over the years, achieved such well deserved popularity that the reviewer has no doubt that this 2nd edition will be equally well recieved by the present generation of chemists.

N. STRAFFORD (Manchester)

A New Periodic Table of the Elements based on the Structure of the Atom, by S. I. TOMKEIEFF, Chapman and Hall Ltd., London, 1954. Price 10*s*. 34 pages.

Parmi les nombreux arrangements de la table périodique des éléments qui nous sont présentés, celui-ci répartit les éléments sur une hélice conique. La justification de cette disposition est donnée, outre les propriétés fondamentales, par des proprétés telles que masse spécifique à l'état solide, dureté des minéraux, composition des météores.

L'ouvrage présente d'abord un rappel de la structure électronique des éléments puis une table des éléments comportant les isotopes, les degrés d'oxydation, la couleur de élément, l'année de sa découverte, l'origine de son nom.

Plusieurs trés belles planches illustrent cet ouvrage très bien présenté sous forme d'album.

G. CHARLOT (Paris)

BUCHBESPRECHUNG

Chronologische Übersichtstabellen (Zur Geschichte der Chemie von den ältesten Zeiten bis zur Gegenwart) von PAUL WALDEN. Springer-Verlag, Berlin, Göttingen, Heidelberg, 1952. xi + 118 Seiten, broschiert DM 12.60.

Der „Nestor der deutschen Chemie" PAUL WALDEN hat die von ihm verfassten chemiegeschichtlichen Werke: *Drei Jahrtausende Chemie* (1944) sowie *Geschichte der Chemie* (1950) durch einen kleinen Band *Chronologischen Übersichtstabellen* ergänzt mit dem Ziel, eine leicht und übersichtliche Darstellung der Chemiegeschichte nach den Hauptdaten zu geben. Nach einer kurz gefassten Einleitung, die sich hauptsächlich mit dem Problem der Ideen, ihrer Bildung und Entwicklung in der Chemie beschäftigt, werden die wichtigen Entdeckungen und Erfindungen in Zeittafeln, eingeteilt in sechs Perioden (I. bis zu Christi Geburt, II. bis 1500; III. 16. und 17. Jahrhundert; IV., V. und VI. 18., 19. und 20. Jahrhundert), gegeben. Die letzten beiden Perioden werden dabei unterteilt in: A. Anorganische und allgemeine Chemie, B. Organische Chemie und C. Analyse der Entwicklung bzw. Rückblick und Ausblick.

Es ist erstaunlich, wie der Verfasser auf Grund seiner vielseitigen Kenntnisse es verstanden hat, in äusserst gewandter und anregender Form auf rund 100 Seiten eine solche Fülle an Stoff zu bieten. Zu diskutieren wäre nur, ob es sinnvoll ist, ohne den erforderlichen zeitlichen Abstand die Entwicklung bis zum Jahre 1951 zu verfolgen, und ob die Auswahl der neuesten Daten nicht einer gewissen Willkür ausgesetzt ist.

Ein jeder Chemiker wird das Werk mit grossem Interesse lesen und sich freuen, die Daten der Chemiegeschichte in so übersichtlicher Form zusammengestellt zu finden. Dass sich P. WALDEN bei seinem hohen Alter von jetzt über 90 Jahren dazu noch bereitgefunden hat, müssen wir ihm ganz besonders danken.

PAUL EHRLICH (Giessen)

STRUCTURE AND BEHAVIOR OF ORGANIC ANALYTICAL REAGENTS

VII. STABILITY OF CHELATES OF 2-(*o*-HYDROXYPHENYL)-BENZIMIDAZOLE AND ANALOGOUS REAGENTS[1]*

by

W. D. JOHNSTON AND H. FREISER

Contribution No. 921 of the Department of Chemistry, University of Pittsburgh, Pa. (U.S.A)

Since previous work in this laboratory has included the measurement of chelate stabilities of 2-(*o*-hydroxyphenyl)-benzoxazole and 2-(*o*-hydroxyphenyl)-benzothiazole[2], it was thought desirable to continue the study of this class of compounds by measuring the stabilities of chelates of 2-(*o*-hydroxyphenyl)-benzimidazole. Of particular interest is the fact that all these reagents are structurally similar to 2-(*o*-hydroxyphenyl)-quinoline which is unusual in that it will not react to form chelates[3]. This effect was presumed to be due to the steric hindrance provided by the benzene portion of the quinoline nucleus. As a further attempt to study this striking effect, stability measurements were made on chelates of 2-(*o*-hydroxyphenyl)-pyridine where no such steric hindrance would be possible. In order to ascertain whether similar steric hindrance is present in chelates of 2-(*o*-hydroxyphenyl)-benzimidazole, stability measurements were made on chelates of 2-(*o*-hydroxyphenyl)-imidazoline.

EXPERIMENTAL

Materials. 2-(*o*-Hydroxyphenyl)-benzimidazole was prepared by the condensation of *o*-phenylenediamine and salicylamide[4]. After recrystallization from a water-alcohol mixture the compound melted at 241-242° C (reported[4] 242° C).

2-(*o*-Hydroxyphenyl)-pyridine was formed through condensation of *o*-methoxyphenyllithium with pyridine, followed by oxidation with nitrobenzene and hydrolysis by hydrobromic and acetic acids[5]. The final product distilled at 135-145° C/2 mm (reported[5] 135-145° C/2 mm).

2-(*o*-Hydroxyphenyl)-imidazoline was prepared in a manner similar to that used by WALTER AND FREISER[4] in preparing 2-(*o*-hydroxyphenyl)-benzimidazole and by CHARLES AND FREISER[6] in preparing 2-(*o*-hydroxyphenyl)-benzothiazole. Equimolar amounts of salicylamide and ethylenediamine were heated together in a distilling flask at 140-150° C for 1.5 hours after which the temperature was raised to 175-185° C for another 1.5 hour period. Both water and ammonia were evolved. The mixture was then distilled in air, over a free flame, at approximately 330° C. After decolorization with charcoal and recrystallization from alcohol and water the product melted at 200-203° C. It was necessary to have the melting point apparatus preheated in this case in order to avoid decomposition below the melting point. A potentiometric titration of this compound with standard sodium hydroxide solution indicated the purity to be 99 ± 1 per cent.

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* Abstracted from the thesis submitted by W. D. JOHNSTON in partial fulfillment of the requirements for the Ph.D. degree at the University of Pittsburgh, August 1953. Present address: Westinghouse Research Laboratories, East Pittsburgh, Pa.

Analysis calculated for $C_9H_{10}N_2O$: N, 17.28
Found: N, 17.23

A somewhat different preparation of this compound appears in the literature[7]. The melting point reported in this work was given as 209° C. The method of purification of dioxane and the procedures used in standardizing metal perchlorate solutions have been previously described[8].

Apparatus, Procedure and Calculations. The titration apparatus and procedure as well as the method of calculating stability constants have been previously described[1,8].

RESULTS

In Table I are listed the acid dissociation constants of the reagents studied in this work. Table II is a tabulation of stepwise chelate formation constants.

TABLE I

ACID DISSOCIATION CONSTANTS IN 50% V/V DIOXANE AND WATER AT 25° C

	pK_{NH}	pK_{OH}
2-(*o*-Hydroxyphenyl)-benzimidazole	4.28	10.76
2-(*o*-Hydroxyphenyl)-imidazoline	6.81	12.80
2-(*o*-Hydroxyphenyl)-pyridine	2.69	12.01
2-(*o*-Hydroxyphenyl)-quinoline	2.07	12.86
1-(*o*-Hydroxyphenyl)-*iso*quinoline	4.38	11.66

TABLE II

CHELATE FORMATION CONSTANTS IN 50%v/v DIOXANE AND WATER AT 25° C

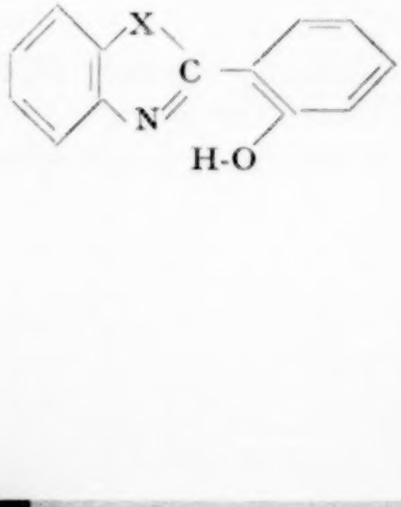
2-(*o*-Hydroxyphenyl)-benzimidazole	log K_1	log K_2	2 log K_{av}
Cu(II)	11.55	9.86	21.40
Ni(II)	7.13	5.67	12.78
Co(II)	7.22	—	(13.70)
Zn(II)	7.90	7.34	15.24
Mn(II)	6.58	—	—
2-(*o*-Hydroxyphenyl)-imidazoline			
Cu(II)	14.64	11.56	26.24
Ni(II)	9.22	8.02	16.98
Zn(II)	9.31	—	(17.24)
2-(*o*-Hydroxyphenyl)-pyridine			
Cu(II)	10.11	8.84	19.00
1-(*o*-Hydroxyphenyl)-*iso*quinoline			
Cu(II)	10.57	—	(19.66)
Ni(II)	(6.45)	—	—

In both Tables I and II certain previously reported data[3] are listed for the purpose of comparison. The numerical values of the previously reported data are slightly different than those reported here since these data were recalculated using corrections to pH meter readings as previously described[1].

All data were obtained in pH regions which previously had been shown to be free of metal hydrolysis[9].

DISCUSSION OF RESULTS

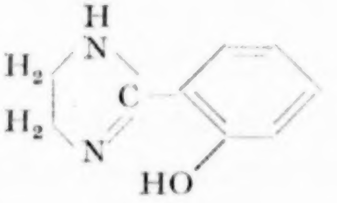
The values of pK_{NH} and pK_{OH} of 2-(*o*-hydroxyphenyl)-benzimidazole can be compared with the values of the constants of 2-(*o*-hydroxyphenyl)-benzoxazole and 2-(*o*-hydroxyphenyl)-benzothiazole[2]. These three compounds can be represented by the general formula:



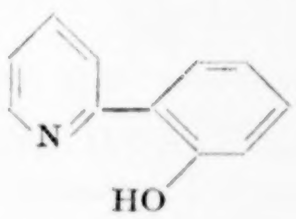
	pK_{NH}	pK_{OH}
2-(*o*-Hydroxyphenyl)-benzoxazole	< 2	11.57
2-(*o*-Hydroxyphenyl)-benzimidazole	4.28	10.76
2-(*o*-Hydroxyphenyl)-benzothiazole	< 2	10.37

where X refers to O, NH, or S. It might be expected that the value of pK_{OH} would inversely related to the electronegativity of X. Actually it was found that the relationship was a direct one. Attempts to relate phenolic acidity to the size of X also gave a relationship which was the reverse of the expected one. In evaluating the pK_{NH} terms it appears that 2-(*o*-hydroxyphenyl)-benzimidazole is the only one of these three reagents having significant basic properties. This is in accord with the findings of ALBERT *et al.*[9] who discussed the basicity of benzimidazole, benzothiazole, and benzoxazole. The factor responsible for the greater basicity of benzimidazole and its derivatives is apparently the base strengthening resonance of the symmetrically protonated benzimidazole species.

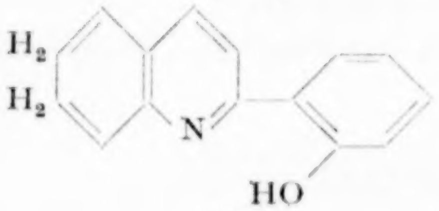
The nitrogen basicity associated with 2-(*o*-hydroxyphenyl)-imidazoline (I) is quite high compared with that of 2-(*o*-hydroxyphenyl)-benzimidazole. This is probably due to the fact that there is no fused benzene ring in the imidazoline compound with which the nitrogen electrons can interact through resonance. However, the base strengthening resonance in the protonated 2-(*o*-hydroxyphenyl)-imidazoline is still possible. The very low acidity of the phenolic group in this compound was not expected and thus far has not been satisfactorily explained.



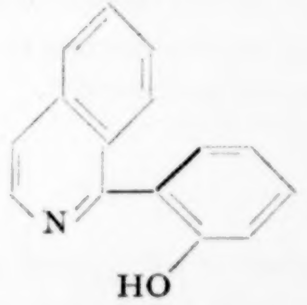
(I)



(II)



(III)



(IV)

Hydrogen bonding probably strongly affects the phenolic acid dissociation constants of 2-(*o*-hydroxyphenyl)-pyridine (II) and 2-(*o*-hydroxyphenyl)-quinoline (III). A favorable charge distribution for hydrogen bonding can be attained through resonance in these reagents. Further, molecular models show that the phenolic hydrogens can approach the nitrogens very closely in both of these compounds. In fact, in completely coplanar configurations, these distances would be slightly less than the distances of closest approach for the non-bonded atoms. This should give rise to very strong hydrogen bonds. The very low phenolic acidities and low nitrogen basicities of these two compounds is in agreement with this picture. The phenolic acidity of 2-(*o*-hydroxyphenyl)-quinoline may be further reduced due to the steric interference of the 8-position of the quinoline nucleus which prevents the approach of hydroxyl ions to the phenolic hydrogen. A molecular model of 1-(*o*-hydroxyphenyl)-*iso*quinoline (IV) has shown that this molecule cannot assume a planar configuration since this would require a superposition of the hydrogen atoms in the 8-position of *iso*quinoline and the 2′-position of the phenyl group. Hence the formation of strong hydrogen bonds is prevented in this compound. This, in addition to the decreased resonance caused by nonplanarity, accounts for the fact that the phenolic group and the reagent nitrogen of this compound have acid and basic character similar to that found in the alkylated 8-hydroxyquinolines.

From Table II it can be seen that the nickel (II) chelate of 2-(*o*-hydroxyphenyl)-benzimidazole is less stable than the corresponding chelates of cobalt (II) and zinc (II). This violation of the normal divalent metal stability sequence, Cu(II) Ni(II) Co(II), Zn(II) Mn(II), has been observed where there are substituent groups on the reagent molecule which might be in position to interfere sterically with chelation[1]. In 2-(*o*-hydroxyphenyl)-benzimidazole the benzene portion of the benzimidazole nucleus might be considered to be in position to offer steric hindrance to chelation in much the same way as does the methyl group in 2-methyl-8-hydroxyquinoline[1]. It should also be noted that the hindered metal stability sequence is found in the chelates of the corresponding benzoxazole compound[2]. Solubility difficulties prevented the establishment of a metal sequence in the case of the benzothiazole reagent[2]. However, in this connection, it is interesting to note that the hindered stability sequence is also found in the chelates of the corresponding benzothiazoline reagent[2]. In all of these reagents there is a substituent group alpha to the heterocyclic nitrogen which might interfere sterically with chelation.

It is interesting to compare the stabilities of chelates formed by the reagents 2-(*o*-hydroxyphenyl)-benzimidazole, 2-(*o*-hydroxyphenyl)-benzoxazole, and 2-(*o*-hydroxyphenyl)-benzothiazole which are described by the general structural formula above. Unfortunately, the only metal for which stability data are available with all three reagents is nickel (II). Figure 1 shows a plot of pK_{OH} against $\log K_{av}$ for the nickel (II) chelates of these reagents. The values for 2-(*o*-hydroxyphenyl)-benzothiazole at 25° C have been estimated from those given at 40° C by assuming that the temperature variations of pK_{OH} and $\log K_{av}$ are the same as those of the benzoxazole compounds. It can be seen that chelate stability is definitely related to the basicity of the phenoxide group in these cases. The fact that the nickel (II) chelate of 2-(*o*-hydroxyphenyl)-benzimidazole is slightly more stable than a straight line would demand is probably due to its relatively more basic nitrogen. However, this trend cannot be attributed completely to reagent basicity since 2-(*o*-hydroxyphenyl)-quinoline (where X in the general structural formula may be taken as -CH=CH-) does not form chelates at all although it has the most basic phenoxide group of the reagents mentioned.

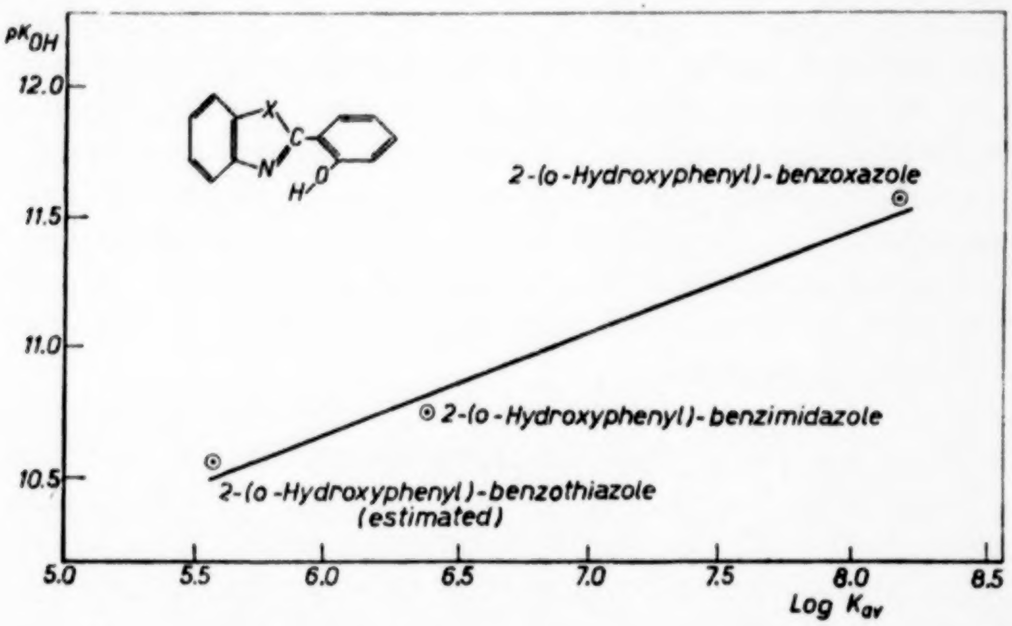


Fig. 1. Log K_{av} *vs.* pK_{OH} for Ni-chelates of reagents of the type indicated.

In this respect it is interesting to consider the effect of the distance between the oxygen and nitrogen of the chelating reagent on chelate stability. If in the general formula shown above we successively introduce O, NH, S, and -CH=CH- into position X, we would expect the jaws of the chelating agent to close slowly due to the increasing size of X. It can be seen that this is the order of decreasing chelate stability. From this it seems reasonable to assume that the metal finds it increasingly difficult to squeeze itself between the ligand groups.

It was hoped that a study of the chelates of 2-(*o*-hydroxyphenyl)-imidazoline would provide another test of the general applicability of the effect of steric hindrance on the metal stability sequence since, in contrast to 2-(*o*-hydroxyphenyl)-benzimidazole, there is no substituent group alpha to the heterocyclic nitrogen. Unfortunately the data obtained in the study of the chelates of this reagent are difficult to interpret. Due to the very high basicity of the reagent, chelation often does not occur until the pH region of metal hydrolysis has been reached. Further, the unusual shape of the $\bar{n}$ curves obtained in some cases are very difficult to explain. It appears that the divalent metal stability sequence in this case is Cu Zn, Ni Co Mn. While the nickel (II) chelate of this reagent is very definitely more stable than the cobalt (II) chelate, as would be expected in an unhindered situation, it is difficult to understand the high order of stability of the zinc (II) chelate.

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It has been previously reported that 2-(*o*-hydroxyphenyl)-quinoline does not react to form chelates[3]. This was ostensibly due to the steric hindrance provided by the hydrogen in the 8-position of the quinoline nucleus. It was expected that when such hindrance was absent such as in the case of 1-(*o*-hydroxyphenyl)-*iso*quinoline and 2-(*o*-hydroxyphenyl)-pyridine chelation would be possible. This was shown to be the case. Because of the fact that most titrations occured in regions of metal hydrolysis it was possible to calculate stability constants for only the copper (II) chelates of the two reagents. The value of log K_1 for the nickel (II) chelate of 1-(*o*-hydroxyphenyl)-*iso*quinoline was estimated by extrapolation. As previously reported, sufficient data were obtained to show that the chelates of 1-(*o*-hydroxyphenyl)-*iso*quinoline exhibit the hindered stability sequence[3]. This was unexpected since there is no substituent group alpha to the heterocyclic nitrogen which could interfere with chelation. However, it should be remembered that steric hindrance in this reagent itself prevents it from assuming a coplanar configuration. Thus, it appears that this type of steric hindrance must exert a similar influence on chelate stability to that which occurs when a blocking group is present. Probably in both cases resonance involving the metal is impaired and the metal-ligand bonds are distorted.

It is difficult to compare the stabilities of the copper (II) chelates of 1-(*o*-hydroxyphenyl)-*iso*quinoline and 2-(hydroxyphenyl)-pyridine since the basicity difference between the two reagents cannot be easily evaluated. Nevertheless, it was somewhat unexpected that these chelates would be of nearly equal stability since the lack of reagent planarity in 1-(*o*-hydroxyphenyl)-*iso*quinoline would be expected to give rise to lower chelate stability than that found in chelates of 2-(*o*-hydroxyphenyl)-pyridine where there is no interference with reagent planarity. The fact that the copper chelates of the two reagents are of about equal stability may be explained by recalling that the nitrogen-oxygen distance in 2-(*o*-hydroxyphenyl)-pyridine is very small. It is quite possible that introduction of a copper (II) ion between these two ligand groups causes distortion of the molecule. Since this would result in the same situation as is found in the copper (II) chelates of 1-(*o*-hydroxyphenyl)-*iso*quinoline, comparable chelate stabilities might be expected.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the U.S. Atomic Energy Commission for this work.

SUMMARY

Stabilities of chelates of 2-(*o*-hydroxyphenyl)-pyridine, 2-(*o*-hydroxyphenyl)-quinoline, 1-(*o*-hydroxyphenyl)-*iso*quinoline, 2-(*o*-hydroxyphenyl)-benzimidazole, and 2-(*o*-hydroxyphenyl)-imidazoline were determined by the Calvin-Bjerrum potentiometric titration technique. The results have been interpreted in terms of steric considerations.

RÉSUMÉ

Les stabilités des chélates de la 2-(*o*-hydroxyphényl)-pyridine, de la 2-(*o*-hydroxyphényl)-quinoline, de la 1-(*o*-hydroxyphényl)-*iso*quinoline, du 2-(*o*-hydroxyphényl)-benzimidazole et de la 2-(*o*-hydroxyphényl)-imidazoline ont été déterminées par la méthode potentiométrique de Calvin-Bjerrum. L'interprétation des résultats est basée sur des considérations stériques.

ZUSAMMENFASSUNG

Die Stabilitäten der Chelate von 2-(*o*-Hydroxyphenyl)-pyridin, von 2-(*o*-Hydroxyphenyl)-chinolin, von 1-(*o*-Hydroxyphenyl)-*iso*chinolin, von 2-(*o*-Hydroxyphenyl)-benzimidazol und von 2-(*o*-Hydroxyphenyl)-imidazolin wurden durch die potentiometrische Methode von Calvin-Bjerrum bestimmt. Die Interpretation der Resultate beruht auf stereochemischen Betrachtungen.

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SENSITIZED SCHIFF'S REAGENT AS AN ACID-BASE INDICATOR

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The use of SCHIFF's reagent for qualitative as well as quantitative estimation of aldehydes[1] is well known. Ethyl alcohol, acetone and other ketones have been shown by HOFFPAUIR *et al.*[2] to sensitize the reagent. According to TOBIE[3], it can also be sensitized by holding the SO_2 content to a minimum and he has extended the use of his sensitized SCHIFF's reagent to the detection of free aldehydic groups in simple aldoses. The present authors have used TOBIE's sensitized SCHIFF's reagent for the estimation of ammonium salts of weak acids[4] and also for the determination of the relative strengths of weak acids[5]. This paper deals with its use as an acid-base indicator.

SCHIFF's reagent contains some amount of free SO_2 as well as loosely bound SO_2 molecules in the fuchsin dye as suggested by WIELAND[6]. Alkalis in moderate amounts bring colouration of the reagent, but an excess suppresses it[7]. It is quite probable that the restoration of colour, which is that of fuchsin itself, in the reagent is due to the neutralization of both free and loosely bound SO_2 molecules. Thus sensitized SCHIFF's reagent shows no colour in acid medium, while in alkaline medium, red colour is developed more or less abruptly, and so the conjugate acid molecule (the reagent) may serve as an indicator, if the acid sto be titrated are much stronger than the former. This principle has been utilized while employing SCHIFF's reagent as an indicator in the neutralization of strong acids by either strong or weak bases.

EXPERIMENTAL

A sample of B.D.H. fuchsin was purified by recrystallization. The other chemicals used were of reagent quality.

The sensitized SCHIFF's reagent was prepared following TOBIE[3], by decolourizing 0.5 g of fuchsin with the calculated amount of H_2SO_3 so as to contain 1 g of SO_2/l and making up the volume to 1000 ml. The light yellow colour remaining after keeping the solution over night was removed with the minimum quantity of activated charcoal.

The spectrophotometric analysis of the coloured solution obtained with alkalis on the reagent showed its characteristic peak at 535 mμ. Measurements of optical densities showed that the intensity of colour suddenly rises to a large value at a particular concentration of the alkali. Hence, if by choosing the proper concentration of this reagent, a strong acid is titrated with a base, the sharp rise in optical density will mark the end-point. In fact, it has been observed that just before the end-point a dull red colour appears which obviously corresponds to the flat portion of the curve relating optical density with concentration of alkali. This dull red colour is replaced by a sudden rise in intensity at the end-point. A few seconds should be allowed before further addition of alkali. The end-points are reproducible and the titre agrees well with those obtained using methyl orange.

Using this indicator the titration is most satisfactory when strong acids are neutralized with either strong or weak bases.

5 ml of the acid (varying between 0.2 - 0.5*N*) and 0.5 ml of the indicator solution were diluted to 25 ml and the titration was carried out by adding quickly the alkali from the burette till a dull red colour is reached. The subsequent additions were made dropwise with a few seconds interval between two additions. The end-point, as stated above, was marked by a sudden sharp increase in intensity of the colour.

The volumes of an ammonium hydroxide solution required to titrate solutions of H_2SO_4, HCl, HNO_3, H_3PO_4, HBr, CCl_3CO_2H according to the above procedure are given in Table I. For comparison the same titrations were done using methyl orange as indicator. These results are also given in the same table. Similar titrations were carried out with a caustic soda solution and the data are given in Table II. Since only the comparison of the titration values were of significance, the actual strengths of the acids and alkalies were not determined.

RESULTS

TABLE I

VOLUME OF NH_4OH IN ml REQUIRED TO NEUTRALIZE 5 ml OF DIFFERENT ACIDS WITH METHYL ORANGE AS WELL AS SENSITIZED SCHIFF'S REAGENT AS INDICATORS

Name of indicator	H_2SO_4	HCl	HNO_3	H_3PO_4	HBr	CCl_3CO_2H
Methyl orange	5.6	6.4	5.1	4.8	5.0	6.3
Sensitized Schiff's reagent	5.55	6.4	5.15	4.75	5.1	6.3

TABLE II

VOLUME OF NaOH IN ml REQUIRED FOR THE NEUTRALIZATION OF 5 ml OF DIFFERENT ACIDS WITH METHYL ORANGE AND SCHIFF'S REAGENT AS INDICATORS

Name of indicator	H_2SO_4	HCl	HNO_3	H_3PO_4	HBr	CCl_3CO_2H
Methyl orange	8.2	7.6	6.4	6.1	5.4	5.6
Schiff's reagent	8.15	7.55	6.42	6.15	5.42	5.6

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DISCUSSION

The agreement between the two sets of titre values shows clearly that the sensitized SCHIFF's reagent can be recommended for neutralization reaction where methyl orange is applicable. The advantage is that the colour transition is sharp; moreover the dull red colour just before the end-point is an added check. Both methyl orange and the sensitized SCHIFF's reagent indicate only the first stage of ionization of phosphoric acid. The pH range at which the sensitized SCHIFF's reagent indicates the colour change lies between 3—5.5. Since there is a lag in the disappearance of red colour of the sensitized SCHIFF's reagent obtaining in alkaline medium on the addition of acid, the reverse titration of that followed here, *viz.* that of adding acid to the alkali which contains the indicator is not satisfactory.

In view of the fact that the colour development of sensitized SCHIFF's reagent is caused by the removal of SO_2 by the alkalis so the amount of the indicator should not be added more than that recommended here. Moreover a sensitized SCHIFF's reagent having greater SO_2 content is also unsuitable in view of its lower sensitivity[4]. Satisfactory titrations are possible with acids ranging in strength from N to $0.1N$; those having lower strengths show variations.

ACKNOWLEDGEMENT

The authors wish to thank Dr. S. K. MUKHERJEE, D.Sc., of Applied Chemistry, Calcutta University for his helpful criticism and Dr. P. C. RAKSHIT, Head of the Department of Chemistry, Presidency College for his help and laboratory facilities.

SUMMARY

The sensitized Schiff's reagent has been used as an indicator in the neutralization of strong acids by means of strong or weak bases.

(1) Since the acid to alkali transition is much sharper than the reverse process, the titration is best done by adding alkali to the acid.

(2) The results are compared with those of titrations using methyl orange as indicator.

(3) The end-point is very sharp with sensitized Schiff's reagent, the transition taking place from a dull red colour to an abrupt rise in intensity.

(4) Acids which are comparable in strengths or weaker than H_2SO_3 cannot be titrated with this reagent as indicator.

RÉSUMÉ

Le réactif de Schiff a été utilisé comme indicateur lors de la neutralisation d'acides forts au moyen de bases fortes et faibles.

1. Le passage de l'acide à la base étant plus net que la réaction inverse, il est donc plus avantageux d'ajouter la base à l'acide.

2. Les résultats sont comparés à ceux obtenus lors de titrations utilisant le méthylorange comme indicateur.

3. Le point final est très net avec le réactif de Schiff. L'intensité de la coloration rouge clair augmente brusquement.

4. Les acides de force égale ou plus faible que SO_3H_2 ne peuvent pas être titrés avec cet indicateur.

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ZUSAMMENFASSUNG

Das Schiffsche Reaktiv wurde als Indikator benützt bei der Neutralisation von starken Säuren mit starken oder schwachen Basen.

1. Da der Übergang von der Säure zur Base deutlicher ist als die entgegengesetzte Reaktion, ist es vorteilhafter, die Säure zur Base zu geben.
2. Die Resultate wurden verglichen mit denjenigen, welche man bei der Titration mit Methylorange als Indikator erhalten hat.
3. Der Umschlagspunkt ist beim Schiffschen Reaktiv sehr deutlich. Die Intensität der hellroten Färbung nimmt sprungweise zu.
4. Die Säuren, welche gleich stark oder schwächer sind als H_2SO_3 können nicht mit Hilfe dieses Indikators titriert werden.

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[5] S. N. BHATTACHARYA AND A. GHOSE, *Anal. Chim. Acta*, 11 (1954) 00.

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STUDIES IN OXIDATION-REDUCTION REACTIONS
I. OXIDATION WITH CHLORAMINE-B, IODINE MONOCHLORIDE METHOD

by

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AFANAS'EV[1] reported that chloramine-B is a good substitute for chloramine-T in analytical chemistry.

In acid medium potassium iodide, arsenious oxide, tartar emetic, mercurous chloride, stannous chloride, potassium thiocyanate, ferrous ammonium sulphate, hydrazine sulphate and hydroquinone react with chloramine-B according to the following equations:

$$KI + C_6H_5SO_2N(Na)Cl + 2\,HCl = KCl + ICl + NaCl + C_6H_5SO_2NH_2$$
$$As_2O_3 + 2\,C_6H_5SO_2N(Na)Cl + 2\,H_2O = As_2O_5 + 2\,NaCl + 2\,C_6H_5SO_2NH_2$$
$$Sb_2O_3 + 2\,C_6H_5SO_2N(Na)Cl + 2\,H_2O = Sb_2O_5 + 2\,NaCl + 2\,C_6H_5SO_2NH_2$$
$$Hg_2Cl_2 + C_6H_5SO_2N(Na)Cl + 2\,HCl = 2\,HgCl_2 + NaCl + C_6H_5SO_2NH_2$$
$$SnCl_2 + C_6H_5SO_2N(Na)Cl + 2\,HCl = SnCl_4 + NaCl + C_6H_5SO_2NH_2$$
$$2\,KCNS + 6\,C_6H_5SO_2N(Na)Cl + 8\,H_2O = 2\,KHSO_4 + 2\,HCN + 6\,NaCl + 6\,C_6H_5SO_2NH_2$$
$$6\,FeSO_4 + 3\,C_6H_5SO_2N(Na)Cl + 6\,HCl = 2\,Fe_2(SO_4)_3 + 2\,FeCl_3 + 3\,NaCl + 3\,C_6H_5SO_2NH_2$$
$$N_2H_4 + 2\,C_6H_5SO_2N(Na)Cl = N_2 + 2\,NaCl + 2\,C_6H_5SO_2NH_2$$
$$C_6H_4(OH)_2 + C_6H_5SO_2N(Na)Cl = C_6H_4O_2 + NaCl + C_6H_5SO_2NH_2$$

EXPERIMENTAL

A known weight of each substance was taken in a conical flask and about 25 ml of water, 20 ml of concentrated hydrochloric acid, 5 ml of 0.02*M* iodine monochloride and 5 ml of chloroform were added to it. The mixture was titrated against standard chloramine-B solution. The reagent was added from a burette until the solution, which was coloured with iodine, became pale yellow and the chloroform layer acquired purple colour. The conical flask was stoppered and vigorously shaken during the titration. Addition of small volumes of the chloramine-B solution was continued, shaking vigorously after each addition, until the chloroform layer was faintly violet. The chloramine-B was then added dropwise, with shaking after the addition of each drop, till the chloroform layer became light pale yellow. The end-point was very sharp.

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[1] B. N. AFANAS'EV, *Sverdlovsk Agr. Inst. Zavodskaya Lab.*, 16 (1950) 1011.

In these titrations normality of the solution with respect to hydrochloric acid was kept between 4*N* to 5*N*. Several titrations were performed in each case. From the volume of chloramine-B used, corresponding to the end-point in each titration, the amount of substance was calculated. The results are recorded in the following tables.

TABLE I

POTASSIUM IODIDE

KI taken g	0.1020*N* Chloramine-B used ml	KI found g
0.0830	9.80	0.0829
0.1245	14.72	0.1245
0.1660	19.62	0.1660
0.2158	25.45	0.2155
0.3735	44.15	0.3737

TABLE II

ARSENIOUS OXIDE

As_2O_3 taken g	0.1020*N* Chloramine-B used ml	As_2O_3 found g
0.0495	9.80	0.0494
0.0891	17.65	0.0890
0.1237	24.35	0.1228
0.1830	36.20	0.1826
0.2374	47.05	0.2373

TABLE III

TARTAR-EMETIC

Tartar-emetic taken g	0.0995*N* Chloramine-B used ml	Tartar-emetic found g
0.1669	10.10	0.1676
0.3338	20.15	0.3346
0.4182	25.20	0.4185
0.5507	33.20	0.5513
0.7520	45.30	0.7523

TABLE IV

MERCUROUS CHLORIDE

Hg_2Cl_2 taken g	0.1000*N* Chloramine-B used ml	Hg_2Cl_2 found g
0.1888	8.00	0.1889
0.2360	10.00	0.2361
0.3540	15.00	0.3541
0.5192	22.00	0.5194
0.7080	29.95	0.7070

TABLE V

STANNOUS CHLORIDE

$SnCl_2.2H_2O$ taken g	0.1000*N* Chloramine-B used ml	$SnCl_2.2H_2O$ found g
0.1130	10.00	0.1128
0.2034	18.00	0.2030
0.2825	25.05	0.2826
0.4068	36.05	0.4067
0.5085	45.07	0.5085

TABLE VI

POTASSIUM THIOCYANATE

KCNS taken g	0.1056*N* Chloramine-B used ml	KCNS found g
0.0162	9.45	0.0162
0.0291	17.00	0.0290
0.0437	25.55	0.0437
0.0583	34.00	0.0582
0.0745	43.57	0.0745

TABLE VII

FERROUS AMMONIUM SULPHATE

$FeSO_4.(NH_4)_2SO_4.6H_2O$ taken g	0.1000*N* Chloramine-B used ml	$FeSO_4.(NH_4)_2SO_4.6H_2O$ found g
0.2352	6.00	0.2351
0.3920	9.97	0.3907
0.5880	14.95	0.5860
0.7056	18.00	0.7055
0.9408	23.95	0.9387

TABLE VIII

HYDRAZINE SULPHATE

$N_2H_4H_2SO_4$ taken g	0.1020*N* Chloramine-B used ml	$N_2H_4H_2SO_4$ found g
0.0325	9.80	0.0326
0.0553	16.75	0.0555
0.0813	24.60	0.0815
0.1105	33.43	0.1107
0.1463	44.25	0.1465

TABLE IX

HYDROQUINONE

$C_6H_4(OH)_2$ taken g	0.1008*N* Chloramine-B used ml	$C_6H_4(OH)_2$ found g
0.0550	9.90	0.0549
0.1155	20.70	0.1147
0.1485	26.78	0.1484
0.1760	31.60	0.1751
0.2475	44.70	0.2477

The results show that the substances given in Tables I to IX can be determined quantitatively by the iodine monochloride method, using chloramine-B as oxidizing agent.

SUMMARY

Chloramine-B has been used as an oxidizing agent in hydrochloric acid medium for the volumetric estimations of potassium iodide, arsenious oxide, tartar-emetic, mercurous chloride, stannous chloride, potassium thiocyanate, ferrous ammonium sulphate, hydrazine sulphate and hydroquinone, using iodine monochloride as a catalyst and pre-oxidizer. Chloroform is used as an indicator. It is coloured pink owing to the liberation of iodine during the titration and becomes light pale yellow at the end-point because of the formation of iodine monochloride.

RÉSUMÉ

La chloramine-B peut être utilisée comme oxydant en solution chlorhydrique, pour le dosage volumétrique des composés suivants: iodure de potassium, anhydride arsénieux, émétique, chlorure de mercure(I), chlorure d'étain(II), thiocyanate de potassium, sulfate de fer(II) et d'ammonium, sulfate d'hydrazine et hydroquinone. On utilise pour cette détermination le monochlorure d'iode comme catalyseur et préoxydant, et le chloroforme comme indicateur. Ce dernier se colore en violet par l'iode libéré pendant la titration et devient jaune pâle au point final par formation de monochlorure d'iode.

ZUSAMMENFASSUNG

Das Chloramin-B kann in salzsaurer Lösung als Oxydationsmittel verwendet werden für die volumetrische Bestimmung folgender Verbindungen: Kaliumjodid, arsenige Säure, Natrium-Kaliumtartrat, Quecksilber(I)chlorid, Zinn(II)chlorid, Kaliumrhodanid, Eisen(II)-ammoniumsulfat, Hydrazinsulfat und Hydrochinon. Für diese Bestimmung verwendet man Jodmonochlorid als Katalysator und voroxydierendes Mittel und das Chloroform als Indikator. Dieses letzte färbt sich violett durch das während der Titration frei gewordene Jod und wird dann schwach gelb beim Endpunkte; dies durch Bildung von Jodmonochlorid.

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STUDIES IN OXIDATION-REDUCTION REACTIONS
II. OXIDATION WITH CHLORAMINE-B
INDIRECT DETERMINATIONS

by

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In the present investigation an attempt has been made to determine indirectly hydrogen peroxide, lead dioxide, manganese dioxide, selenium dioxide, sodium formate, sodium sulphide, sodium metavanadate, potassium iodate and copper sulphate by a volumetric method, using chloramine-B as an oxidizing agent.

In all titrations with chloramine-B, 5 ml of 0.02*M* iodine monochloride, 5 ml of chloroform and enough of hydrochloric acid to keep its normality between 4*N* to 5*N* were added to the titrant in a conical flask. Chloramine-B was added from a burette until the solution, which was coloured with iodine, became pale yellow. The conical flask was then stoppered and vigorously shaken. Addition of small volumes of chloramine-B solution was continued, shaking vigorously after each addition, until the chloroform layer was faintly violet. The reagent was then added dropwise, with shaking after the addition of each drop, until the chloroform layer changed its colour from violet to light pale yellow. The end-point was very sharp.

Determintion of hydrogen peroxide

Hydrogen peroxide reacts with arsenious oxide in alkaline medium:

$$As_2O_3 + 2\ H_2O_2 = As_2O_5 + 2\ H_2O$$

A known weight of hydrogen peroxide was taken in a conical flask and a known excess of arsenious oxide dissolved in ten per cent. sodium hydroxide solution was added to it. The mixture was allowed to stand for a couple of minutes and acidified with concentrated hydrochloric acid. 5 ml of 0.02*M* iodine monochloride and 5 ml of chloroform were added to it. The conical flask was stoppered and the mixture was vigorously shaken. The excess of arsenious oxide, left unreacted in the mixture, was determined by titrating it against standard chloramine-B solution.

$As_2O_3 + 2\ C_6H_5SO_2N\ (Na)Cl + 2\ H_2O = As_2O_5 + 2\ C_6H_5SO_2NH_2 + 2\ NaCl$

The results are given in Table I.

TABLE I

HYDROGEN PEROXIDE

H_2O_2 taken	$N/10$ As_2O_3 added	$N/10$ Chloramine-B used for excess As_2O_3	$N/10$ As_2O_3 used by H_2O_2	H_2O_2 found
g	ml	ml	ml	g
0.0187	15.00	4.00	11.00	0.0187
0.0243	17.00	2.75	14.25	0.0242
0.0312	20.00	1.65	18.35	0.0312
0.0565	36.00	2.80	33.20	0.0565
0.0788	50.00	3.60	46.40	0.0789

Determination of dioxides of lead and manganese

Potassium iodide reacts with the dioxides in presence of concentrated hydrochloric acid:

$$KI + PbO_2 + 4\ HCl = PbCl_2 + KCl + ICl + 2\ H_2O$$
$$KI + MnO_2 + 4\ HCl = MnCl_2 + KCl + ICl + 2\ H_2O$$

In presence of hydrochloric acid, potassium iodide reacts with chloramine-B:

$$KI + C_6H_5SO_2N(Na)Cl + 2\ HCl = KCl + NaCl + ICl + C_6H_5SO_2NH_2$$

A known weight of the dioxide was taken in a conical flask and a known excess of potassium iodide solution was added to it. The mixture was acidified with hydrochloric acid to keep its normality between $4N$ to $5N$. 5 ml of $0.02M$ iodine monochloride and 5 ml of chloroform were added to it. The excess of iodide was titrated back with standard chloramine-B solution. The results are given in Tables II and III.

TABLE II

LEAD DIOXIDE

PbO_2 taken	$M/20$ KI added	$N/10$ Chloramine-B used for excess KI	$M/20$ KI used by PbO_2	PbO_2 found
g	ml	ml	ml	g
0.0430	8.00	4.40	3.60	0.0430
0.1290	15.00	4.20	10.80	0.1291
0.1316	20.00	9.00	11.00	0.1316
0.1824	25.00	9.70	15.30	0.1829
0.2584	30.00	8.40	21.60	0.2583

TABLE III

MANGANESE DIOXIDE

MnO_2 taken	$M/20$ KI added	$N/10$ Chloramine-B used for excess KI	$M/20$ KI used by MnO_2	MnO_2 found
g	ml	ml	ml	g
0.0325	10.00	2.52	7.48	0.0325
0.0480	20.00	8.95	11.05	0.0480
0.0848	25.00	5.50	19.50	0.0848
0.1168	30.00	3.15	26.85	0.1169

Determination of selenium dioxide

Selenium dioxide reacts with hydrazine sulphate according to the equation:

$$SeO_2 + N_2H_4 = Se + N_2 + 2\ H_2O$$

In acid medium hydrazine sulphate reacts with chloramine-B:

$$N_2H_4 + 2\ C_6H_5SO_2N\ (Na)Cl = N_2 + 2\ NaCl + 2\ C_6H_5SO_2NH_2$$

A known weight of selenium dioxide was dissolved in minimum quantity of hot water and a known excess of $M/10$ hydrazine sulphate solution was added to it. The mixture was heated to boiling. Selenium that separated was removed by filtration. The unused hydrazine sulphate in the filtrate was titrated against standard chloramine-B in presence of hydrochloric acid, 5 ml of $0.02M$ iodine monochloride and 5 ml of chloroform. The results are recorded in Table IV.

TABLE IV

SELENIUM DIOXIDE

SeO_2 taken	$M/10$ $N_2H_4H_2SO_4$ added	$N/10$ Chloramine-B used for excess $N_2H_4H_2SO_4$	$M/10$ $N_2H_4H_2SO_4$ used by SeO_2	SeO_2 found
g	ml	ml	ml	g
0.0777	10.00	12.00	7.00	0.0777
0.0999	12.00	12.00	9.00	0.0999
0.1330	15.00	12.00	12.00	0.1332
0.1660	20.00	20.00	15.00	0.1665
0.2040	25.00	26.40	18.40	0.2042

Determination of sodium formate

Sodium formate reduces mercuric chloride to mercurous chloride:

$$HCOONa + 2\ HgCl_2 = Hg_2Cl_2 + NaCl + HCl + CO_2$$

In presence of hydrochloric acid, chloramine-B oxidizes mercurous chloride to mercuric chloride:

$$Hg_2Cl_2 + C_6H_5SO_2N\,(Na)Cl + 2\,HCl = 2\,HgCl_2 + NaCl + C_6H_5SO_2NH_2$$

A known weight of sodium formate was taken in a conical flask. Some sodium acetate solution, an excess of saturated mercuric chloride solution and enough of water to make the volume to about 75 ml were added to it. The mixture was heated on a steam bath for about two hours until the whole of carbon dioxide was evolved. The flask was cooled and the precipitated mercurous chloride filtered. The precipitate along with the filter paper was transferred to a conical flask, and titrated against standard chloramine-B solution after the addition of hydrochloric acid, iodine monochloride and chloroform. The results are given in Table V.

TABLE V

SODIUM FORMATE

HCOONa taken	*N*/10 Chloramine-B used	HCOONa found
g	ml	g
0.0136	4.00	0.0136
0.0204	6.00	0.0204
0.0340	10.00	0.0340
0.0476	14.05	0.0478
0.0680	19.95	0.0678

Determination of sodium sulphide

Sodium sulphide reacts with arsenious oxide in presence of hydrochloric acid:

$$3\,Na_2S + As_2O_3 + 6\,HCl = As_2S_3 + 6\,NaCl + 3\,H_2O$$

Arsenious oxide is oxidised to arsenic oxide by chloramine-B in acid medium:

$$As_2O_3 + 2\,C_6H_5SO_2N\,(Na)Cl + 2\,H_2O = As_2O_5 + 2\,NaCl + 2\,C_6H_5SO_2NH_2$$

1.5000 g of sodium sulphide were dissolved in 100 ml of water and a known excess of arsenious oxide (2.5058 g) dissolved in sodium hydroxide was added to it. The mixture was thoroughly stirred and acidified with dilute hydrochloric acid, when yellow precipitate of arsenious sulphide was formed. The precipitate was filtered, washed with water and the filtrate made up to 250 ml. The excess of arsenious oxide present in the filtrate was determined by titrating it against standard chloramine-B after the addition of hydrochloric acid, iodine monochloride and chloroform. The results are tabulated in Table VI.

TABLE VI

SODIUM SULPHIDE

Na_2S taken	Filtrate taken for titration	*N*/10 Chloramine-B used for As_2O_3	As_2O_3 in 250 ml of filtrate	As_2O_3 used by Na_2S	Na_2S found
g	ml	ml	g	g	g
1.5000	20.00	20.00	1.2370	1.2688	1.5000
	20.00	20.00			
	20.00	20.05			
	20.00	20.00			

Determination of sodium metavanadate

Sodium metavanadate reacts with hydrazine sulphate in hydrochloric acid medium:

$$N_2H_4 + 4\ NaVO_3 + 12\ HCl = 4\ VOCl_2 + 4\ NaCl + 8\ H_2O + N_2$$

In presence of hydrochloric acid, chloramine-B oxidizes hydrazine sulphate:

$$N_2H_4 + 2\ C_6H_5SO_2N\ (Na)Cl = 2\ NaCl + 2\ C_6H_5SO_2NH_2 + N_2$$

A known weight of sodium metavanadate was taken in a conical flask, a known excess of standard hydrazine sulphate solution and enough of concentrated hydrochloric acid to keep the normality of acid between (7*N* to 7.5*N*) were added. The mixture was vigorously shaken. The excess of hydrazine sulphate left unreacted was titrated back with standard chloramine-B after the addition of iodine monochloride and chloroform. The results are recorded in Table VII.

TABLE VII

SODIUM METAVANADATE

$NaVO_3$ taken	*M*/40 $N_2H_4H_2SO_4$ added	*N*/10 Chloramine-B used for excess $N_2H_4H_2SO_4$	*M*/40 $N_2H_4H_2SO_4$ used by $NaVO_3$	$NaVO_3$ found
g	ml	ml	ml	g
0.1221	18.00	8.00	10.00	0.1220
0.2198	25.00	7.00	18.00	0.2196
0.3050	30.00	5.00	25.00	0.3050
0.3904	40.00	8.00	32.00	0.3904
0.4880	45.00	4.98	40.02	0.4882

Determination of potassium iodate

Potassium iodate reacts with arsenious oxide in presence of hydrochloric acid:

$$As_2O_3 + KIO_3 + 2\,HCl = As_2O_5 + KCl + H_2O + ICl$$

In hydrochloric acid medium chloramine-B reacts with arsenious oxide:

$$As_2O_3 + 2\,C_6H_5SO_2N(Na)Cl + 2\,H_2O = As_2O_5 + 2\,NaCl + 2\,C_6H_5SO_2NH_2$$

A known amount of potassium iodate was taken in a conical flask and a known excess of arsenious oxide dissolved in ten per cent. sodium hydroxide solution was added to it. The mixture was acidified with concentrated hydrochloric acid to keep the normality between $4N$ to $5N$. The mixture was vigorously shaken. The excess of arsenious oxide left unreacted was titrated back with standard chloramine-B solution after the addition of iodine monochloride and chloroform. The results are given in Table VIII.

TABLE VIII

POTASSIUM IODATE

KIO_3 taken	M/40 As_2O_3 added	N/10 Chloramine-B used for excess As_2O_3	M/40 As_2O_3 used by KIO_3	KIO_3 found
g	ml	ml	ml	g
0.0249	12.00	7.35	4.65	0.0249
0.0356	15.00	8.35	6.65	0.0356
0.0498	20.00	10.68	9.32	0.0499
0.0642	25.00	13.00	12.00	0.0642
0.0783	30.00	15.35	14.65	0.0784

Determination of copper sulphate

A known weight of copper sulphate was dissolved in water and saturated with sulphur dioxide gas. The solution was boiled and a known excess of standard potassium thiocyanate was added to it.

$$2\,CuSO_4 + 2\,KCNS + SO_2 + 2\,H_2O = Cu_2(CNS)_2 + 2\,H_2SO_4 + K_2SO_4$$

The precipitated copper thiocyanate was filtered. The filtrate was boiled in an atmosphere of CO_2 till free from sulphur dioxide gas, diluted with water to a known volume and titrated against standard chloramine-B after the addition of hydrochloric acid, iodine monochloride and chloroform.

$$2\,KCNS+6\,C_6H_5SO_2N(Na)Cl+8\,H_2O=2\,KHSO_4+6\,NaCl+6\,C_6H_5SO_2NH_2+2\,HCN$$

The results are given in Table IX.

TABLE IX

COPPER SULPHATE

$CuSO_4.5H_2O$ taken	$M/60$ KCNS added	$N/10$ Chloramine-B used for excess KCNS	$M/60$ KCNS used by $CuSO_4.5H_2O$	$CuSO_4.5H_2O$ found
g	ml	ml	ml	g
0.0416	20.00	10.00	10.00	0.0416
0.0499	25.00	13.05	11.95	0.0497
0.0603	30.00	15.40	14.60	0.0607
0.0832	35.00	15.10	19.90	0.0829
0.1248	40.00	10.00	30.00	0.1248

From the results given in Tables I to IX, it is evident that chloramine-B can be used as a volumetric reagent to estimate indirectly, hydrogen peroxide, lead dioxide, manganese dioxide, selenium dioxide, sodium formate, sodium sulphide, sodium metavanadate, potassium iodate and copper sulphate.

SUMMARY

Chloramine-B has been used as an oxidizing agent in hydrochloric acid medium for the indirect volumetric estimations of hydrogen peroxide, lead dioxide, manganese dioxide, selenium dioxide, sodium formate, sodium sulphide, sodium metavanadate, potassium iodate and copper sulphate using iodine monochloride as a catalyst and pre-oxidiser. Chloroform is used as an indicator. It is coloured pink owing to the liberation of iodine during the titration and becomes light pale yellow at the end-point because of the formation of iodine monochloride.

RÉSUMÉ

La chloramine-B peut être utilisée comme oxydant, en solution chlorhydrique, pour le dosage volumétrique indirect des composés suivants: peroxyde d'hydrogène, bioxyde de plomb, bioxyde de manganèse, bioxyde de sélénium, formiate de sodium, sulfure de sodium, métavanadate de sodium, iodate de potassium et sulfate de cuivre. On utilise pour cette détermination le monochlorure d'iode comme catalyseur et préoxydant, et le chloroforme comme indicateur. Ce dernier se colore en violet par l'iode libéré pendant la titration et devient jaune pâle au point final, par formation de monochlorure d'iode.

ZUSAMMENFASSUNG

Das Chloramin-B kann in salzsaurer Lösung als Oxydationsmittel verwendet werden für die indirekte volumetrische Bestimmung folgender Verbindungen: Wasserstoffperoxyd, Bleidioxyd, Magnesiumdioxyd, Selendioxyd, Natriumformiat, Natriumsulfid, Natriummetavanadate Kaliumjodat, Kupfersulfat. Für diese Bestimmung wird das Jodmonochlorid als Katalysator und voroxydierendes Mittel, und das Chloroform als Indikator verwendet. Dieses letzte färbt sich violett durch das während der Titration frei gewordene Jod und wird dann schwach gelb beim Endpunkte; dies durch Bildung von Jodmonochlorid.

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RAPID DETERMINATION OF THORIUM IN ORES
II. ESTIMATION OF TRACE AMOUNTS OF THORIUM IN COMPLEX MINERALS AND ORES

by

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The determination of thorium in minerals and ores as iodate by potassium iodate[1] or by iodate-oxalic acid mixture[2] fails when it is present in trace amounts owing to interference with sulphuric acid, and the solubility losses in high nitric acid concentration. For trace estimation of thorium, FRIMALDI AND FAIRCHILD[3] have used a procedure which is essentially the chemical concentration of thorium followed by its estimation (a) nephelometrically as iodate for quantities less than 1 mg of thorium (b) photometrically with pararsonic acid or (c) gravimetrically as oxide if more than 1 mg of thorium is indicated. FAHEY AND FOSTER[4], after obtaining the iodate in pure form, estimated thorium indirectly by reduction of the iodate with hypophosphorous acid in acid medium followed by photometric estimation of iodine extracted in carbon tetrachloride. Iodometric titration has also been recommended.

The above methods use rather large amounts of ore (about 5 g for 0.04 per cent. thorium is recommended) and in the case of minerals like ilmenite, columbite-tantalite and samarskite they can be used only after considerable time has been spent in opening up the mineral. Further, the use of mercurous nitrate as a carrier for thorium fluoride, and its subsequent volatilization at the controlled temperature, is not a simple manipulation.

The essential features of the method now proposed are: (a) opening of the mineral with sodium peroxide (b) precipitation of thorium as phosphate along with zirconium or titanium, without prior removal of silica (c) treatment of the precipitate with hydrofluoric acid to remove silica by volatilization, to form soluble fluorides with interfering elements and to scavenge thorium as fluoride using lanthanum as carrier (d) precipitation of thorium as iodate in potassium iodate-oxalic acid mixture and (e) its estimation by titrating against thiosulphate, the iodine liberated in acid solution.

EXPERIMENTAL

The procedure as outlined above was first tried on pure thorium and thorium-zirconium mixtures in order to establish the optimum conditions as regards volumes and concentration of reagents.

General procedure

1. A 1-gram sample is cautiously fused in a nickel crucible with 5-6 g of sodium peroxide, the mass being kept in a liquid state for about 10 minutes. The crucible is cooled and transferred to a 250-ml beaker. About 100 ml of cold water is added and the melt is disintegrated. The crucible is removed and rinsed, first with water and then with hydrochloric acid (1:1) and the rinses are added to the solution.

2. The solution is neutralized with hydrochloric acid (1:1) and then 10 ml of excess hydrochloric acid (1:1) are added. The contents of the beaker are digested on the steam bath, and 10 mg of zirconium oxide are added in the form of nitrate. (If titanium and zirconium are already present in the sample, which can be noticed from the amount of precipitate before addition of zirconium as carrier, it is not necessary to add zirconium.) The solution is warmed to about 90° C. 4 g of diammonium phosphate dissolved in about 20 ml of water are added and the solution is diluted with water to 200 ml. The beaker is covered and its contents are digested on the steam bath for at least 2 hours.

3. The solution is stirred and filtered on Whatman No. 540, 11 cm paper. The precipitate is then washed with 4 per cent. ammonium nitrate solution.

4. The precipitate is then transferred to a 100 ml platinum dish. The paper is burnt in a platinum crucible and the ash added to the dish.

5. 20 ml of hydrofluoric acid are added and digested on the steam bath, while stirring with a platinum rod, and the solution is evaporated until about 8 ml remain. 10 ml of hydrofluoric acid are again added and the solution is re-evaporated to about 8 ml and then diluted with 30 ml of water.

6. The solution is warmed on the steam bath and 10 mg of lanthanum oxide, in the form of nitrate are added. The solution is stirred with a platinum rod and allowed to stand overnight at room temperature.

7. The solution is filtered on a Whatman No. 40, 9 cm filter paper in a hard rubber or plastic funnel. The precipitate is washed twice with 10 to 15 ml of 5 per cent. hydrofluoric acid wash solution. The precipitate is then washed twice with water.

8. The paper together with the precipitate is transferred back to the dish and carefully heated so that the product chars but does not ignite. When fumes are no longer evolved the contents are heated at 900° C until carbon is burnt off.

9. The residue in the dish is carefully wetted with a few drops of water. 0.5 ml of sulphuric acid and one drop of hydrofluoric acid are carefully added and the dish is heated on the hot plate for about 25 minutes until dry. Then the dish is heated over a low Bunsen flame below 450° C until no more fumes appear.

10. 15 ml of concentrated nitric acid are added to the dish and the solution is evaporated to dryness on water bath. This is repeated two or three times, stirring with a glass rod, until all the thorium is in solution.

11. Finally 2 ml of nitric acid (1:1) are added and the solution is transferred to a 50 ml beaker by means of a jet of water and the dish "bobbied" thoroughly. 3 ml of potassium iodate (15 per cent. in 1:1 nitric acid) and 0.5 ml of oxalic acid (10 per cent.) are added and the volume of solution is made to 25 ml. Filter paper

TABLE I

DETERMINATION OF THORIUM IN COMPLEX MINERALS AND ORES AND SYNTHETIC MIXTURES

S. No.	Mineral	Thorium oxide added mg	Thorium oxide		Remarks
			taken mg	found mg	
A	Ilmenite	—	—	0.11	Ilmenite obtained after magnetic separation of monazite. Radiometric assay: 0.2 per cent. of monazite sand
		0.3	0.41	0.407	
		0.6	0.71	0.715	
B	Ilmenite	—	—	0.088	Ilmenite processed to free it from radioactive minerals; Radiometric assay; slightly less than sample *A*
		0.3	0.388	0.383	
		0.6	0.688	0.650	
		0.9	0.988	0.950	
		1.2	1.288	1.220	
C	—	—	1.1*	0.99	*Value by usual iodate procedure. Mineral not fully analysed but contained 0.11 per cent. thoria and a little uranium oxide
		0.5	1.49	1.45	
D	Samarskite	—	16.0*	15.7	*Value by usual iodate procedure. Mineral high in $(Cb+Ta)_2O_5$, TiO_2, U_3O_8 and rare earths; thoria 1.6 per cent.
E	Columbite-Tantalite	—	—	0.66	75.9 per cent. $(Cb+Ta)_2O_5$ 1.28 per cent. TiO_2 with little uranium oxide and rare earths
		0.2	0.86	0.84	
		0.4	1.06	1.02	
F	Synthetic mixture containing zirconium	0.2	0.2	0.198	Containing 10 mg of ZrO_2
		0.4	0.4	0.407	
		0.8	0.8	0.792	
G	Synthetic mixture containing tin	0.5	0.5	0.484	Containing 1 g $SnCl_2{,}2H_2O$ and 0.5 mg ThO_2
		0.5	0.5	0.495	

pulp is added to the solution and the solution is cooled in ice cold water for about half an hour.

12. The supernatant liquid is decanted through a Whatman No. 42, 4 cm paper and finally the precipitate is transferred to the paper using a fine jet of 76 per cent. ice cold alcohol. (80 ml of 95 per cent alcohol diluted with distilled water to 100 ml and cooled in ice cold water.) The paper is washed three times with the alcohol solution. Total washings should not exceed 25 ml. The precipitate, along with the filter paper, is transferred to the beaker and treated with 2 ml of sulphuric acid (1:1). This brings acid into contact with all parts of paper.

After about five minutes 20 ml of water are added and the solution is stirred until a fine pulp is formed. 5 ml of potassium iodide (10 per cent.) are added and the iodine liberated is titrated against 0.01*N* sodium thiosulphate, using starch solution as indicator. 1 ml of 0.01*N* thiosulphate is equivalent to 0.11 mg of thorium oxide.

A number of complex minerals like ilmenite, samarskite and columbite-tantalite have been analysed by the same common procedure as described above and the results obtained on a 1 g sample are given in Table I also along with the results obtained on a few synthetic mixtures.

In samples *A*, *B*, *D* and *E* it was not found necessary to add zirconium nitrate as a carrier. The volume of the precipitate obtained, though large, did not offer any difficulties in subsequent operation.

DISCUSSION

Very complex minerals like ilmenite, columbite-tantalite etc. have been analysed with great care within a short period of two working days. With 1 g sample it is possible to estimate up to 0.01 per cent. thorium with a reasonable accuracy of 5 per cent. For still lower percentages of thorium it would not be difficult to apply the method with a larger amount of sample, *i.e.*, 2 g, while for minerals which are of a simpler nature some of the steps in the recommended procedure could be omitted or suitably modified. Higher quantities of thorium up to 2.5 per cent. could also be analysed titrimetrically by the procedure suggested in this paper.

SUMMARY

A very rapid method for the estimation of trace amounts of thorium up to 0.01 per cent. or thereabouts even in complex minerals like ilmenite and columbite-tantalite has been described. Thorium is collected in an acid solution with phosphates of zirconium and titanium without prior separation of silica, after decomposition of the mineral with sodium peroxide. Thorium is next collected as fluoride with lanthanum as a carrier, precipitated as thorium iodate in potassium iodate-oxalic acid mixture and finally titrated against 0.01*N* sodium thiosulphate. Accurate results are obtained within a short time of two working days.

RÉSUMÉ

Une méthode très rapide est proposée pour le dosage de traces de thorium jusqu'à 0.01%, même dans les minerais complexes tels que l'ilménite et la colom bite-tantalite. Le thorium est entraîné en solution acide avec les phosphates de zirconium et de titane, sans séparation préalable de la silice, après désagrégation du minerai par le peroxyde de sodium. Le thorium est ensuite séparé comme fluorure, en présence de lanthane, précipité comme iodate de thorium par le mélange iodate de potassium - acide oxalique et finalement titré par le thiosulfate de sodium 0.01 *N*. Des résultats précis sont obtenus rapidement: en deux jours environ.

ZUSAMMENFASSUNG

Es wird eine sehr schnelle Methode vorgeschlagen fur die Bestimmung von Thorium bis zu 0.01% selbst in komplexen Mineralien wie in Ilmenit und in Columbit-Tantalit. Das Thorium wird nach einem Aufschluss mit Natriumperoxyd, in saurem Milieu in Lösung gebracht mit Zirkonium- und Titanphosphat, ohne vorherige Abtrennung des Siliciums. Dann wird das Thorium als Fluorid abgetrennt, in Gegenwart von Lanthan als Thoriumiodat gefällt mit dem Gemisch Kaliumjodat-Oxalsäure, und mit Natriumthiosulfat 0.01 *N* titriert. Man erhält auf diese Weise schnell genaue Resultate: ungefähr in zwei Tagen.

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ESTIMATION OF METALS AS SULPHIDES

II. ESTIMATION OF PLATINUM METALS

by

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One of the well-known methods for the estimation and separation of the platinum metals consists in precipitating them as sulphides from hydrochloric acid solution. The method gives fairly correct results but is not convenient, for hydrogen sulphide has to be passed into a hot solution for a considerable time. Thus in the case of iridium for example, hydrogen sulphide has to be passed into the solution at about 90° C for about three hours to precipitate the sulphide and even then the precipitation may not be complete and the filtrate may have to be treated again with the gas for ensuring complete precipitation of the metal. Not only does the complete precipitation of the sulphides take considerable time, but the precipitate obtained under these conditions is generally of a sticky character and cannot be removed easily from the beaker. It cannot be weighed directly. It must be ignited and converted into the metal either directly or by reduction of the oxide formed on ignition by a current of hydrogen.

In a series of papers[1,2] from this laboratory it has been shown that many metals can be precipitated very easily and quickly as sulphides by decomposing their thiosalts and some of these sulphides can be weighed directly for the estimation of the metal. In the case of platinum, however, it was found[3] that though the metal is precipitated by decomposing the thiosalt with hydrochloric acid, the precipitated sulphide could not be weighed directly, but had to be ignited first to convert it into the metal before the precipitate was weighed.

Further investigations were made subsequently in order to find out whether it was possible to obtain platinum sulphide in a form in which it could be weighed directly. It was ultimately found that if the thiosalt formed by adding excess of alkali sulphide is decomposed with acetic acid in presence of a large quantity of ammonium acetate the precipitated sulphide cannot only be filtered very easily, but is in such a condition that it can be weighed directly for the estimation of the metal.

The method of treatment with alkali sulphide followed by excess of acetic acid and ammonium acetate was then applied to the other platinum metals and was found to be successful in the case of all except osmium. In the case of all the four metals — iridium, rhodium, ruthenium and palladium — the precipitated sulphide can be filtered very easily in a sintered glass crucible and after washing with alcohol and ether weighed directly without heating. The weight of the metal can be obtained by multiplying the weight of the precipitate by a known factor.

EXPERIMENTAL

Estimation of platinum as sulphide

Solutions containing platinum were prepared by dissolving platinic chloride in water and standardized by reduction to metal with formic acid[4] and also by decomposing the thiosalt with hydrochloric acid and igniting the precipitated sulphide to metal[5]. Measured portions of this solution were made slightly alkaline with sodium hydroxide solution and then treated with a large excess of 2*N* sodium sulphide reagent. The clear solution containing the thiosalt was acidified with a large excess of acetic acid and 5-10 grams of ammonium acetate was then added. The mixture was boiled for 1-2 minutes, allowed to cool and then again brought to the boiling point. After this treatment the precipitate of sulphide settled very well on cooling to the room temperature. Cooling in ice cold water hastens the settling. The precipitate was filtered through a weighed sintered glass crucible (porosity 4) at a very low pressure, washed first thoroughly with water and then with alcohol and ether successively. It was then sucked dry at the filter pump for 5 minutes, dried in a vacuum desiccator for half an hour and weighed. The ratio: weight of the metal/weight of the precipitated sulphide is 0.5588 corresponding exactly with the formula $PtS_2,5H_2O$. If the precipitate is heated at 130°-135° C constant weight is obtained but the value of the ratio in this case is 0.6610 corresponding with $PtS_2,2H_2O$. The weights of metallic platinum in the measured portion of the solution and those corresponding with the precipitate actually obtained are given in Tables I & II.

TABLE I

DETERMINATION OF PLATINUM WITH 2*N* SODIUM SULPHIDE REAGENT WASHING WITH ALCOHOL AND ETHER, DRYING AT 15°—20° C.

No.	Vol of Pt solution in ml	Vol of reagent added in ml	Vol of 8*N* acetic acid added in ml	Wt. of ppt. sulphide in g	Wt. of Pt in the ppt. in g	Wt. of Pt actually present in g
1	25	40	40	0.0658	0.03676	0.03676
	25	50	50	0.0658	0.03676	
2	20	40	45	0.0526	0.02939	0.02941
	20	50	55	0.0526	0.02939	
3	50	50	55	0.0546	0.03051	0.03051
	50	60	70	0.0546	0.03051	
4	25	60	80	0.1890	0.1056	0.1056
	25	65	85	0.1890	0.1056	

TABLE II

DETERMINATION OF PLATINUM WITH $2N$ SODIUM SULPHIDE REAGENT
WASHING WITH ALCOHOL AND ETHER, DRYING AT 130°—135° C

No.	Vol of Pt solution in ml	Vol of reagent added in ml	Vol of $8N$ acetic acid added in ml	Wt. of ppt. sulphide in g	Wt. of Pt in the ppt. in g	Wt. of Pt actually present in g
1	25	40	40	0.0556	0.03676	0.03676
	25	50	50	0.0556	0.03676	
2	20	40	45	0.0445	0.02942	0.02941
	20	50	55	0.0445	0.02942	
3	50	50	65	0.0462	0.03054	0.03051
	50	60	70	0.0462	0.03054	
4	25	60	80	0.1598	0.1056	0.1056
	25	65	85	0.1598	0.1056	

Estimation of iridium as sulphide

The most reliable method for the estimation of iridium depends upon its precipitation as sulphide from a hot solution containing 20% hydrochloric acid by volume. The precipitate is strongly ignited, the oxidized residue is heated and cooled in a current of hydrogen and weighed as metal. The method is not convenient for reasons given previously.

Solutions containing iridium on treatment with alkali sulphide form a clear solution. This solution on heating with excess of hydrochloric acid becomes turbid but the precipitate does not settle. The substitution of acetic acid for hydrochloric acid and the addition of a large quantity of ammonium acetate results in the complete precipitation of the metal as sulphide which settles easily and can be washed and weighed directly.

For estimating iridium as sulphide a solution of iridium sodium chloride (Kahlbaum's) was prepared in water and standardized by the method referred to above. Measured portions of this solution were treated with a large excess of alkali sulphide reagent followed by large excess of acetic acid and ammonium acetate. The mixture was boiled and cooled as in the case of platinum. The precipitate of iridium sulphide was filtered through a weighed sintered glass crucible (porosity 4) at a very low pressure, washed first thoroughly with water containing 5% alcohol (otherwise precipitate tends to pass through the filter) then with alcohol and ether successively. It was then sucked dry at the filter pump for 5 minutes, dried in a vacuum desiccator for half an hour and weighed. The ratio: weight of the metal/weight of the precipitated sulphide is 0.5830 corresponding exactly with the formula $Ir_2S_3,10H_2O$. The precipitate was heated up to 85° C but the weight remained constant.

The weights of the metallic iridium in the measured portions of the solution and those corresponding with the precipitate actually obtained are given in Tables III, IV and V.

TABLE III

DETERMINATION OF IRIDIUM WITH CONCENTRATED AMMONIUM SULPHIDE REAGENT

No	Vol of Ir solution in ml	Volume of reagent added in ml	Vol of glacial acetic acid added in ml	Wt. of ppt. sulphide in g	Wt. of Ir in the ppt. in g	Wt. of Ir actually present in g
1	2	20	25	0.0190	0.01108	0.01108
	2	25	30	0.0190	0.01108	
	2	30	40	0.0189	0.01103	
2	5	20	25	0.0410	0.02391	0.02391
	5	25	30	0.0410	0.02391	
	5	30	40	0.0409	0.02379	
3	10	25	30	0.0644	0.03755	0.03755
	10	30	35	0.0644	0.03755	
	10	35	40	0.0643	0.03749	

TABLE IV

DETERMINATION OF IRIDIUM WITH $1N$ AMMONIUM SULPHIDE REAGENT

No.	Vol of Ir solution in ml	Vol of reagent added in ml	Vol of $4N$ acetic acid added in ml	Wt. of ppt. sulphide in g	Wt. of Ir in the ppt. in g	Wt. of Ir actually present in g
1	2	15	15	0.0189	0.01103	0.01108
	2	20	20	0.0190	0.01108	
	2	25	25	0.0190	0.01108	
2	5	30	25	0.0409	0.02379	0.02391
	5	35	30	0.0410	0.02391	
	5	40	35	0.0409	0.02379	
3	10	30	30	0.0644	0.03755	0.03755
	10	35	35	0.0643	0.03749	
	10	40	40	0.0643	0.03749	

TABLE V

DETERMINATION OF IRIDIUM WITH $2N$ SODIUM SULPHIDE REAGENT

No.	Vol of Ir solution in ml	Vol of reagent added in ml	Vol of $4N$ acetic acid added in ml	Wt. of ppt. sulphide in g	Wt. of Ir in the ppt. in g	Wt. of Ir actually present in g
1	2	15	15	0.0189	0.01103	0.01108
	2	20	20	0.0190	0.01108	
	2	25	25	0.0190	0.01108	
2	5	30	30	0.0410	0.02391	0.02391
	5	35	35	0.0409	0.02379	
	5	40	40	0.0410	0.02391	
3	10	30	30	0.0644	0.03755	0.03755
	10	35	35	0.0644	0.03755	
	10	40	40	0.0643	0.03749	

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Estimation of rhodium as sulphide

Rhodium, like platinum, is generally estimated by precipitating it as sulphide[7] from a hot solution containing hydrochloric acid. The precipitate in this case is finally ignited in a current of hydrogen to convert the oxide into metal and then weighed. It can also be precipitated as metal by formic acid[8] in alkaline solution or by magnesium in acid solution[9]. In all these cases the precipitate has to be ignited and cooled in a current of hydrogen before being weighed.

A careful study of the behaviour of rhodium salts with sodium sulphide and acetic acid has shown that the precipitate of the sulphide after suitable treatment can be weighed as such or it may be ignited in a current of hydrogen and weighed as metal. Ammonium sulphide cannot be used, as the precipitate formed with this reagent does not settle and has a tendency to pass through the filter.

For estimating rhodium as sulphide a solution containing rhodium was prepared by dissolving rhodium sodium sesqui-chloride (Kahlbaum's) in water and dilute hydrochloric acid. It was standardized by all the three methods mentioned above. Measured portions of this solution were made just alkaline with ammonium hydroxide and then treated with a large excess of sodium sulphide reagent. A large excess of acetic acid and ammonium acetate were then added and the mixture boiled for 5-10 minutes to complete the precipitation of the sulphide. The mixture was then cooled to the room temperature to allow the precipitate to settle (cooling in ice-cold water hastens the settling of the precipitate) and filtered through a weighed sintered glass crucible (porosity 4) at a very low pressure. The precipitate was washed thoroughly with water containing 5% alcohol, then with alcohol and ether successively, sucked dry at the filter pump, dried in a vacuum desiccator for half an hour and weighed. The ratio: weight of the metal/weight of the precipitated sulphide is 0.5225 and corresponds exactly with the formula $Rh_2S_3,3H_2S$ which is a well-known compound. The precipitated sulphide can also be ignited in a current of hydrogen and weighed as metal.

TABLE VI

DETERMINATION OF RHODIUM WITH 2N SODIUM SULPHIDE REAGENT FOLLOWED BY WASHING WITH ALCOHOL AND ETHER

No.	Vol of Rh solution in ml	Vol of reagent added in ml	Vol of 5N acetic acid added in ml	Wt. of ppt. sulphide in g	Wt. of Rh in the ppt. in g	Wt. of Rh actually present in g
1	25	40	50	0.0436	0.02278	0.02276
	25	50	60	0.0436	0.02278	0.02276
	20	40	50	0.0349	0.01824	0.01824
2	25	45	60	0.0760	0.03971	0.03970
	25	55	70	0.0760	0.03971	0.03970
	20	45	60	0.0608	0.03177	0.03176
3	25	40	50	0.0857	0.04478	0.04478
	25	60	70	0.0857	0.04478	

TABLE VII

DETERMINATION OF RHODIUM WITH $2N$ SODIUM SULPHIDE REAGENT FOLLOWED BY IGNITION OF THE SULPHIDE IN HYDROGEN AND COOLING IN THE SAME

No.	Vol of Rh solution in ml	Vol of reagent added in ml	Vol of $5N$ acetic acid added in ml	Wt. of Rh after ignition of the sulphide ppt. in g	Wt. of Rh actually present in g
1	25	40	50	0.0227	0.02276
	25	50	60	0.0227	0.02276
	20	40	50	0.0182	0.01824
2	25	45	60	0.0397	0.03970
	25	55	70	0.0397	0.03970
	20	45	60	0.0317	0.03176
3	25	40	50	0.0447	0.04478
	25	60	70	0.0447	0.04478

The weights of the metallic rhodium contained in a measured portion of the solution and those corresponding with the precipitate actually obtained are given in Tables VI and VII.

Estimation of ruthenium as sulphide

Ruthenium can be precipitated as sulphide[10] by passing hydrogen sulphide in a hot solution containing 5% hydrochloric acid. Precipitation is very slow. The precipitate of sulphide is ignited at a high temperature, then reduced in a current of hydrogen and weighed as metal. Another method consists in precipitating ruthenium as metal[11] from an alkaline solution by boiling with absolute alcohol. The precipitated metal is ignited and cooled in a current of hydrogen and weighed.

If ruthenium sulphide is precipitated by treating the solution with sodium sulphide and acetic acid successively it can be weighed directly after washing with alcohol and ether and the whole estimation completed in about three hours. The precipitate of sulphide can also be ignited in a current of hydrogen and weighed as metal, the usual precautions being taken for preventing deflagration or explosion.

For estimating ruthenium as sulphide, ruthenium chloride (Kahlbaum's) was dissolved in dilute hydrochloric acid and the solution standardized by the methods mentioned above. Measured portions of the solution were made slightly alkaline with ammonium hydroxide then treated with a large excess of sodium sulphide reagent followed by acetic acid in excess and 5-10 grams ammonium acetate. The mixture was boiled for 1-2 minutes, cooled and again heated to boiling. The precipitate of sulphide which settled very well on cooling was filtered through a weighed sintered glass crucible (porosity 4) at a very low pressure, washed with water, alcohol and ether successively, sucked dry at the filter pump, dried in a vacuum desiccator for half an hour and weighed. The ratio: weight of the metal/weight of the precipitated sulphide was found to be 0.6064 corresponding exactly with the formula $Ru_2S_3,2H_2O$. The weights of metallic ruthenium contained in a measured portion of the solution and those corresponding with the precipitate actually obtained are given in Tables VIII and IX.

TABLE VIII

DETERMINATION OF RUTHENIUM WITH 2*N* SODIUM SULPHIDE REAGENT FOLLOWED BY WASHING WITH ALCOHOL AND ETHER

No.	Vol of Ru solution in ml	Vol of reagent added in ml	Vol of 8*N* acetic acid added in ml	Wt. of ppt. sulphide in g	Wt. of Ru in the ppt. in g	Wt. of Ru actually present in g
1	25	45	50	0.0745	0.04519	0.04520
	20	60	70	0.0596	0.03614	0.03616
	10	50	55	0.0298	0.01807	0.01808
2	25	55	65	0.1420	0.08612	0.08616
	20	60	75	0.1136	0.06890	0.06893
	10	45	60	0.0568	0.03444	0.03446

TABLE IX

DETERMINATION OF RUTHENIUM WITH 2*N* SODIUM SULPHIDE REAGENT FOLLOWED BY IGNITION OF THE SULPHIDE IN HYDROGEN AND COOLING IN THE SAME

No.	Vol of Ru solution in ml	Vol of reagent added in ml	Volume of 8*N* acetic acid added in ml	Wt. of Ru after igniting the sulphide ppt. in g	Wt. of Ru actually present in g
1	25	45	50	0.0452	0.04520
	25	55	60	0.0452	
	20	50	60	0.0361	0.03616
	20	60	70	0.0361	
2	25	55	65	0.0861	0.08616
	25	60	70	0.0861	
	20	55	70	0.0689	0.06893
	20	60	75	0.0689	

Estimation of palladium as sulphide

The most satisfactory method for the estimation of palladium consists in precipitating it with dimethylglyoxime[12] in presence of 2-3*N* hydrochloric acid. The precipitate is generally allowed to stand overnight before filtration. It is very bulky and not more than 0.1 gram of the metal can be taken for an estimation. The precipitation of palladium as sulphide from an acid solution and ignition to the metal can be used only for the estimation of very small quantities of the metal, because the sulphide is apt to fuse to globules from which sulphur cannot be removed completely by ordinary ignition.

The method in which palladium is precipitated as sulphide by treatment with alkali sulphide and acetic acid successively, and weighed as sulphide after washing with alcohol and ether, gives as accurate results as the dimethylglyoxime method but takes less time. It is possible to complete the estimation in 2-3 hours.

For the estimation of palladium as sulphide a solution containing the metal was prepared by dissolving palladium chloride (B.D.H.) in dilute hydrochloric acid and standardized by the dimethylglyoxime method. Measured portions of this solution were made just neutral by adding ammonium hydroxide, and then treated with excess of alkali sulphide reagent, followed by a large excess of acetic acid and ammonium acetate. The mixture was heated to boiling, allowed to stand for 15-20 minutes and the precipitate of palladium sulphide filtered through a weighed sintered glass crucible (porosity 4) at a low pressure. After washing with hot water, alcohol and ether successively, the precipitate was sucked dry at the filter pump dried in a vacuum desiccator for half an hour and weighed. The ratio: weight of the metal/weight of the precipitated sulphide was found to be 0.6108 corresponding exactly with the formula $PdS,2H_2O$. The weights of metallic palladium contained in a measured portion of the solution and those corresponding with the precipitate actually obtained are given in Tables X and XI.

TABLE X

DETERMINATION OF PALLADIUM WITH 1*N* AMMONIUM SULPHIDE REAGENT

No.	Vol of Pd solution in ml	Vol of reagent added in ml	Vol of 4*N* acetic acid added in ml	Wt. of ppt. sulphide in g	Wt. of Pd in the ppt. in g	Wt. of Pd actually present in g
1	25	40	50	0.0074	0.00452	0.00453
	25	45	55	0.0074	0.00452	
2	25	35	45	0.0709	0.04331	0.04332
	25	40	50	0.0709	0.04331	
3	25	40	45	0.1112	0.06794	0.06794
	25	45	50	0.1112	0.06794	
4	25	40	50	0.0672	0.04106	0.04106
	25	50	60	0.0672	0.04106	

When 1*N* ammonium sulphide reagent was replaced by concentrated ammonium sulphide quite good results were obtained.

TABLE XI

DETERMINATION OF PALLADIUM WITH 2*N* SODIUM SULPHIDE REAGENT

No.	Vol of Pd solution in ml	Vol of reagent added in ml	Vol of 4*N* acetic acid added in ml	Wt. of ppt. sulphide in g	Wt. of Pd in the ppt. in g	Wt. of Pd actually present in g
1	25	40	50	0.0074	0.00452	0.00453
	25	45	55	0.0074	0.00452	
2	25	35	40	0.0709	0.04331	0.04332
	25	40	45	0.0709	0.04331	
3	25	35	45	0.1112	0.06794	0.06794
	25	40	50	0.1112	0.06794	
4	25	40	45	0.0672	0.04106	0.04106
	25	45	50	0.0672	0.04106	

Note on the behaviour of osmium

When solutions containing osmium were treated with alkali sulphide solution and acetic acid successively and the precipitate obtained is weighed the weight was found to be too low.

SUMMARY

1. It has been shown that all the platinum metals with the exception of osmium can be estimated as sulphide if the solution containing the metal is treated with a large excess of alkali sulphide followed by excess of acetic acid and ammonium acetate. The precipitate of the sulphide can be washed with water, alcohol and ether successively, dried in a vacuum desiccator, and weighed.

2. By the above procedure it is possible to complete the analysis for all the platinum metals within 3 hours, whereas the procedures described in the literature require much longer time —in many cases more than 24 hours.

3. The precipitates obtained by the older procedures were very sticky and difficult to filter. By carrying out the precipitation in the presence of acetic acid and ammonium acetate it has been possible to obtain the precipitate in an easily filterable form.

4. The above method not only provides a very convenient general method of estimating the platinum metals, but also throws interesting light on the formation of thiosalts and the precipitation of sulphides by their decomposition.

RÉSUMÉ

1. Il est démontré que les métaux du groupe du platine, à l'exception de l'osmium, peuvent être dosés comme sulfures si la solution à analyser est traitée par un gros excès de sulfure alcalin, puis par un excès d'acide acétique et d'acétate d'ammonium. Le précipité de sulfures est lavé à l'eau, à l'éther successivement, puis séché dans un dessicateur à vide et pesé.

2. Par ce procédé, il est possible d'effectuer le dosage de tous les métaux du platine en 3 heures, tandis que les méthodes décrites dans la littérature exigent beaucoup plus de temps, souvent plus que 24 heures.

3. Les précipités obtenus par les anciennes méthodes sont très gélatineux et difficiles à filtrer. En effectuant la précipitation en présence d'acide acétique et d'acétate d'ammonium, on peut obtenir un précipité se filtrant facilement.

4. La méthode décrite ne constitue pas seulement un procédé avantageux pour le dosage des métaux du platine, mais elle apporte également des éclaircissements sur la formation des thiosels et la précipitation des sulfures par leur décomposition.

ZUSAMMENFASSUNG

1. Es wird gezeigt, dass die Metalle der Platingruppe, mit Ausnahme des Osmiums, als Sulfide dosiert werden können, sofern die zu analysierende Lösung mit einem grossen Überschuss von Alkalisulfiden, dann mit einem Überschuss an Essigsäure und Ammoniumacetat behandelt wird. Der Sulfidniederschlag wird mit Wasser, dann mit Alkohol und zum Schlusse mit Äther gewaschen und anschliessend in einem Dessikator (bei Unterdruck) getrocknet. Dann wird er gewogen.

2. Mit dieser Technik ist es möglich, die Bestimmung aller Platinmetalle in 3 Stunden durchzuführen, während die in der Literatur beschriebenen Methoden viel mehr Zeit beanspruchen, oft sogar mehr als 24 Stunden.

3. Die Niederschläge, welche mit den alten Methoden erhalten werden, sind sehr gallertig und schwer zu filtrieren. Bei der Ausfällung in Gegenwart von Essigsäure und Ammoniumacetat, kann man einen leicht filtrierbaren Niederschlag erhalten.

4. Die beschriebene Methode ist nicht nur ein vorteilhaftes Verfahren zur Bestimmung der Metalle der Platingruppe, sondern trägt auch dazu bei, die Bildung von Thiosalzen und das Ausfällen von Sulfiden durch deren Zersetzung zu klären.

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THE OXINATES OF THORIUM AND SOME CERITE EARTHS

by

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8-Hydroxy quinoline (oxine) is a very valuable analytical reagent and despite its nonspecificity has found wide application. It gives under varying pH conditions precipitates with all metals precipitated by ammonia. HECHT AND REICH-ROHRWIG[1] obtained two varieties of thorium oxinate, yellow and red, with a composition corresponding to $Th(C_9H_6ON)_4$ and $Th(C_9H_6ON)_4.C_9H_7ON$ respectively. While the yellow form is precipitated at 50° and below, the orange variety separates at 70° or above and is stable up to 170°. FRERE[2] and FRITZ[3] have confirmed these observations.

PIRTEA[4] precipitated lanthanum with the reagent from strongly ammoniacal solution and showed that the precipitate was $La(C_9H_6ON)_3$. BERG AND BECKER[5] similarly determined cerous cerium and separated thorium from Ce^{+3} by precipitating the former in the presence of acetic acid. Several of the rare earths are also reported to have been estimated with oxine by MANNELLI[6] and MELENT'EV AND TEREKHOVKO[7] but details are lacking.

According to GOTO[8] the precipitation of thorium oxinate starts at pH 3.7 and is complete between 4.4 and 12.5. In the present investigation the precipitation of the oxinates of Th and some of the cerite earths has been studied in detail and by a control of pH, Th has been separated from the other rare earths. The pH values where the oxinates of the cerite earths are completely precipitated lie so near to each other that a separation of one from the other is not possible. Further, the structures of the two oxinates of thorium have been studied. From evidence of extinction coefficients it has been shown that the two oxinates are distinct compounds.

The pH values have been determined with a cambridge bench type direct reading pH meter with a glass electrode coupled to a dip-type saturated calomel element. Sufficient time, about 15 min, was allowed for the glass electrode to reach equilibrium before measurement. The meter was fed from a 12 volt accumulator of large capacity and set with a standard buffer at pH 3.97. Little variation of the setting was noticed during a run of several hours. The scale was also checked, occasionally by measurement against standard buffer at pH 3.1.

EXPERIMENTAL

The thorium solution was a pure sample available in the laboratory[8].

The cerium solution was also of high grade purity yielding on ignition a pale yellowish residue with no discolouration.

The lanthanum solution was of similar purity. The test employed for the absence of other rare earth elements was the snow-white colour of the oxide on ignition.

The nitrate solutions of the elements were first analysed for the rare earth contents by precipitation as oxalates, ignition and final weighing as oxides. Thus:

10 ml of	Th	solution contained	0.0733 g of ThO_2
,,	Ce	,, ,,	0.0835 g of CeO_2
,,	La	,, ,,	0.1191 g of La_2O_3

The oxine solution was prepared by dissolving a weighed quantity of the material (B.D.H. AnalaR) in a definite amount of glacial acetic acid and diluting so as to give a 5% solution of the reagent in 3% acid.

The precipitation of the oxinates with variation in pH was studied as follows:— In a 400 ml pyrex beaker, 10 ml of the thorium or rare earth solution were diluted to 100 ml and 20 ml of the reagent were then added. Dilute ammonia (*N*/10) was run dropwise from a burette until a slight but permanent turbidity was observed. During the addition the mixture was stirred mechanically. Addition of ammonia was then stopped and after a further 15 min of stirring, the pH of the solution was read. (This gave the pH of incipient precipitation.) A further quantity of ammonia was added to produce appreciable precipitation. The pH was read and the amount of the element precipitated was determined by filtering, washing with 0.5% reagent adjusted to the pH of the precipitant and igniting to the oxide. Several determinations were thus made at different pH values until precipitation was complete. The results are shown in Table I A, B and C.

TABLE I

EFFECT OF pH ON THE PRECIPITATION OF THORIUM AND CERTAIN RARE EARTH ELEMENTS WITH OXINE

A. Thorium

Weight of ThO_2 taken = 0.0733 g

pH of solution	Amount of ThO_2 precipitated
3.5 (Turbidity appears)	0.0111
3.5	0.0113
3.61	0.0483
3.70	0.0673
3.85	0.0733
4.01	0.0732

B. Cerium

Weight of Ce(III) taken as CeO_2 = 0.0835 g

pH of solution	Amount of CeO_2 precipitated g
4.44 (Turbidity appears)	—
4.48	0.0230
4.80	0.0553
5.22	0.0812
5.55	0.0836
5.80	0.0835

C. Lanthanum

Weight of La_2O_3 taken = 0.1191 g

pH of solution	Amount of La_2O_3 precipitated g
4.8 (Turbidity appears)	0.0036
5.27	0.0961
5.50	0.1142
5.75	0.1191
5.90	0.1190

Thus the precipitation of thorium is complete at pH 3.85, of Ce(III) at 5.55, of La at 5.75. The precipitation of Ce(III) starts at 4.4, and of La at about 4.8, all well above that for the complete precipitation of thorium. For the separation of thorium and rare earths two series of experiments were carried out, one at pH 3.9 and the other at pH 4.1. At both pH values, the rare earth solutions were first added individually to the thorium solution and finally in a mixture. The results are shown in Table II.

While separation at pH 3.9 is quite efficient, at pH 4.1 there is fair contamination which however is not large enough to rule out complete removal after a second precipitation.

Double precipitation at pH 4.1

The precipitate was partially washed and returned with the filter to the original beaker. It was then digested with a small amount of 1 ; 1 HCl until solution was complete and the filter disintegrated into pulp. The excess acid was neutralized with a little ammonia, more reagent was added and the precipitation was completed by adjusting the pH to 4.1. Under these conditions the thorium residue was now white and showed no over weight, as is evident from Table II B.

TABLE II

SEPARATION OF RARE EARTHS FROM THORIUM WITH OXINE

A. Single precipitation

Weight of ThO_2 taken = 0.0733 g

Rare earth	Weight added	Wt. of ThO_2 ppted. g at pH 3.9	Diff. in mg	at pH 4.1	Diff. in mg
Ce(III) as CeO_2	0.0835	0.0734	+0.1	0.0750	+1.7
La_2O_3	0.0442	0.0733	—	0.0741	+0.8
(CeO_2 + La_2O_3)	0.1277	0.0735	+0.2	0.0800	+6.7

B. Double precipitation with oxine at pH 4.1

ThO_2 taken = 0.0733 g

Rare earth	Weight added g	Weight of ThO_2 precipitated g	Diff. in mg
Ce(III) as CeO_2	0.0835	0.0734	+0.1
La_2O_3	0.0442	0.0733	—
(CeO_2 + La_2O_3)	0.1277	0.0735	+0.2

C. Separation of thorium from monazite

Weight of ThO_2 present in 10 ml = 0.0351 g

1. Single precipitation with oxine at pH 3.9

Weight of ThO_2 present, g	Weight of ThO_2 found, g	Diff. in mg	Remarks
0.0351	0.0382	+3.1	Residue coloured
0.0351	0.0383	+3.2	,,

2. Double precipitation at pH 3.9

Weight of ThO_2 present, g	Weight of ThO_2 found, g	Diff. in mg	Remarks
0.0351	0.0353	+0.2	Practically colourless
0.0351	0.0352	+0.1	,,

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THE STRUCTURE OF THE OXINATES OF THORIUM

The orange thorium oxinate on drying at 170° C decomposes, leaving behind the yellow complex. This behaviour suggests that the orange red variety may be a loose molecular compound. Such a compound on solution in solvents like hydrochloric acid would break up, while in solvents like acetone, chloroform, etc. it is more likely to retain its complex structure. A spectrophotometric study of the two complexes in different solvents is therefore likely to reveal these differences.

This study in HCl, acetone, CCl_4, $CHCl_3$ and toluene is detailed below. The two forms of thorium oxinate were precipitated following HECHT AND REICH-ROHRWIG[1] and dried to constant weight at 110° C. The formula assigned to each form was confirmed, both by igniting a weighed sample to the oxide as well as bromometric titration of the oxine groups.

Weighed quantities of the two complexes and the reagent were separately dissolved in the respective solvents and suitably diluted to give the desired concentration. The solutions were then scanned in a Beckmann Quartz UV spectrophotometer in matched 1 cm thick cornig glass cells in the spectral range 420 mμ to 300 mμ. A tungsten filament lamp run on a large capacity 6 V battery of accumulators served as source of light from 420 mμ to 350 mμ. Between 350 mμ and 300 mμ a hot cathode hydrogen lamp was employed. The slit width was adjusted between 0.02 to 0.04 mm on the dial, always maintaining spectral purity — the effective band width thus varies from 0.3 to 0.6. Transmission readings were taken against the solvent in all cases. The amounts of the yellow and red complexes were so chosen that the same quantity of thorium was present in both. The extinctions were then calculated to 1 g mole per 1000 ml of Th in the complex. Thorium is known to have no absorption in the region studied.

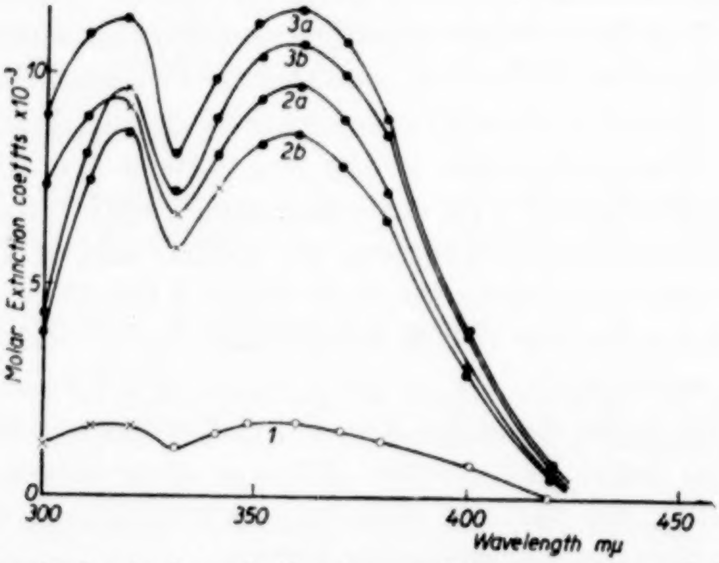

Fig. 1. Spectrochemical study of thorium-oxine complex. Solvent 0.1N HCl: Curve 1 — Reagent; Curve 2a — Red complex; Curve 3a — Yellow complex. Solvent 0.5N HCl: Curve 1 — Reagent; Curve 2b — Red complex; Curve 3b — Yellow complex.

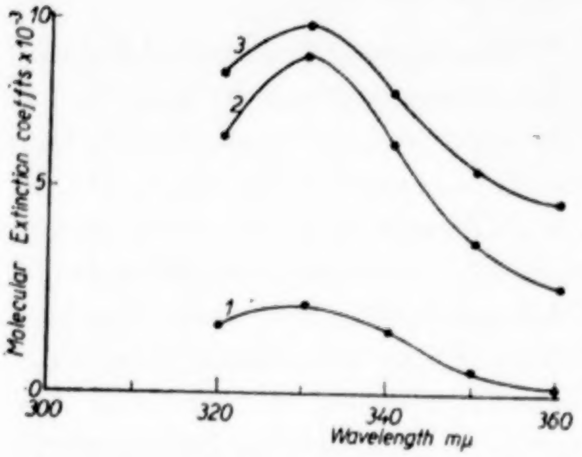

Fig. 2. Spectrochemical study of thorium-oxine complex. Solvent acetone: Curve 1 — Reagent; Curve 2 — Yellow complex; Curve 3 — Red complex.

Molar extinction coefficients of the reagent have also been measured in the several solvents for comparison. These results are plotted in Fig. 1, 2. While BEER's law was obeyed in hydrochloric acid and acetone, in the other organic solvents there were appreciable variations. In Tables III, IV and V are shown the molecular extinction coefficients.

While in acetone the red complex showed higher absorption of the two, in dilute HCl the reverse was the case. Further it is interesting to compare the molar extinction coefficients at the two concentrations of HCl. While the reagent shows no change in absorption, with increase in acidity the absorption of the yellow complex as well as the red complex registers a fall. The fall is great in the case of the red complex. In 0.5*N* HCl the absorption of the red complex is just what would be due to five oxine groups. This suggests that already at this concentration of HCl, the complex has broken down into its constituents. This leads to the conclusion that the basic structure of the red complex cannot be $Th(C_9H_6ON)_4$, C_9H_7ON but $Th(C_9H_6ON)_5$ which is less stable and breaks up into Th and 5 oxine molecule as the concentration of acid increases. The four complex is more stable. Further light is thrown by studies in other solvents. While the deviations from BEER's law in these solvents are too large to justify any quantitative deductions, yet comparisons at similar or corresponding concentrations yield results of value. In Table IV are recorded extinction coefficients calculated from observations at two or more not widely differing concentrations of the different species in the various solvents. The extinctions of the red variety are also compared with the extinctions of mixture of Th-4 oxinate complex with 1 mole of oxine. It will be seen that in toluene and chloroform, the extinctions of Th-5 oxine complex do not show any significant variation from those of the Th-4 oxine + oxine mixture. In carbon tetrachloride on the other hand the 5 complex shows a higher absorption as in acetone.

Thus the evidence so far discussed shows that the four and five oxine complexes of thorium are two distinct structures. While in some solvents like acetone and carbon tetrachloride, the distinct structure of the five complex is maintained, in other solvents there is a dissociation into

$$Th(OX)_5 \rightarrow Th + 5(OX)$$

in strongly ionic solvents like dil. HCl, and in others like chloroform, the dissociation is probably

$$Th(OX)_5 \rightarrow Th(OX)_4 + (OX)$$

As the investigation has neared completion, it is interesting to note a communication on the subject by MOELLER AND VENKATARAMANIAH[10], where-in the authors conclude that while the $Th(OX)_5$ is a definite entity in the crystalline state, on solution in chloroform the complex breaks up into $Th(OX)_4$ + OX.

TABLE III

MOLAR EXTINCTION COEFFICIENTS
Solvent hydrochloric acid

	0.1*N* HCl			0.5*N* HCl		
Wave length	*Oxine	*Yellow	*Red	*Oxine	*Yellow	*Red
420	109	763	626	111	701	690
400	549	3861	3173	574	3647	2791
380	1280	8894	7415	1287	8771	6566
370	1564	10769	9015	1570	10050	7935
360	1695	11700	9809	1709	10807	8508
350	1635	11346	9438	1637	10501	8321
340	1420	9852	8274	1450	9039	7265
330	1158	8086	6730	1224	7200	5801
320	1631	11325	9300	1696	9756	8880
310	1554	11000	9000	1629	8244	7765
300	1281	9050	7385	1300	4391	4023

* Mean of three observations,
at concentrations
[1] Reagent 1.10^{-4} to 4.10^{-4} molar. $1\cdot10^{-4}$ to $4\cdot10^{-4}$ molar.
[2] Thorium $2\cdot5.10^{-5}$ to $1\cdot10^{-4}$ molar. $2\cdot5.10^{-5}$ to $1\cdot10^{-4}$ molar.

Spectrophotometric estimation of thorium as oxinate

Thorium is precipitated with oxine as the four complex, the precipitate is dissolved in 0.1*N* HCl or acetone and estimated by measuring the absorption at 320 mμ in 0.1*N* HCl and 330 mμ in acetone. In both cases as little as 0.002 mg of the oxide per ml may be estimated with fair accuracy. A working curve was obtained by treating different quantities of Th with oxine and dissolving the precipitate in definite volumes of the solvent. The working curves are shown in Fig. 3. Test estimations were made with two different thorium solutions as well as monazite extract with the results shown in Table VI.

TABLE IV

MOLECULAR EXTINCTION COEFFICIENTS*

	Solvent: Acetone				Solvent: Carbon tetrachloride			
Wave length	Reagent	Yellow comp.	Yellow + one mole reagent	Red comp.	Reagent	Yellow comp.	Yellow + one mole reagent	Red comp.
310	—	—	—	—	2169	9510	11800	14550
320	1624	5974	7710	7591	2370	10150	12600	15250
330	2088	8085	11150	8820	2250	9370	11650	13150
340	1511	6047	7615	7160	1760	6935	8800	10370
350	517	3601	4235	5294	995.0	4805	6001	6025
360	130	2571	2804	4625	—	—	—	—

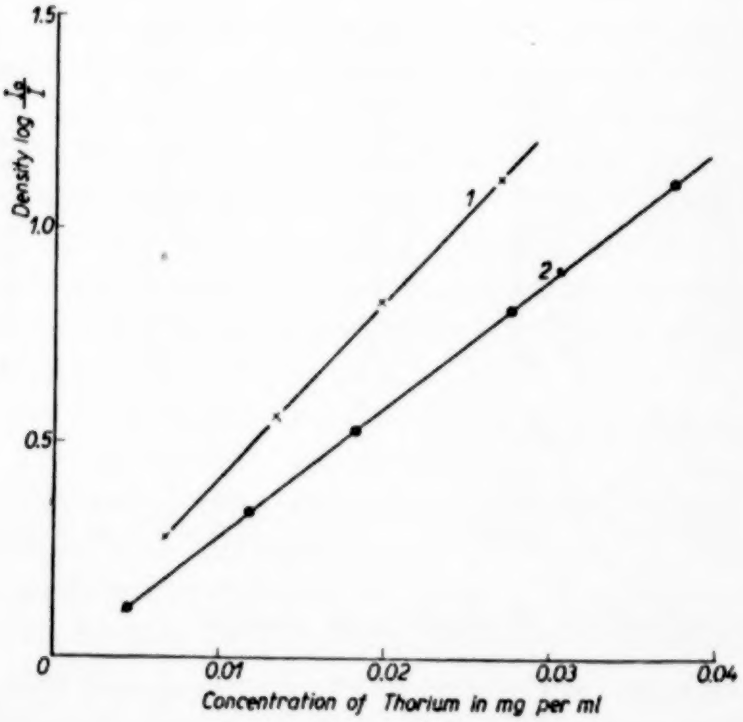

Fig. 3. Calibration curves:
1. BEER's law plot of thorium oxinate in hydrochloric acid at 320 mμ.
2. BEER's law plot of thorium oxinate in acetone at 330 mμ.

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* Mean of three observations
at concentrations
[1] Reagent $2.76 \cdot 10^{-4}$ to $1.380 \cdot 10^{-3}$ molar. $1.38 \cdot 10^{-4}$ to $2.07 \cdot 10^{-4}$ molar.
[2] Thorium $6.93 \cdot 10^{-5}$ to $1.386 \cdot 10^{-4}$ molar. $2.91 \cdot 10^{-5}$ to $5.82 \cdot 10^{-5}$ molar.

TABLE V

MOLECULAR EXTINCTION COEFFICIENTS*

	Solvent — Chloroform				Solvent — Toluene			
Wave length	Reagent	Yellow comp.	Yellow + one mole reagent	Red comp.	Reagent	Yellow comp.	Yellow + one mole reagent	Red comp.
310	2910	11040	14100	13700	2330	10990	13400	12440
315	2680	11680	14450	14830	2335	11015	13565	13525
320	2585	11640	14300	15380	2340	11310	13700	13600
330	2260	10460	12800	12820	2037	10120	12200	11910
340	1475	8168	9700	10430	1950	7850	9100	8950

* Mean of three observations

[1] Reagent $1.724 \cdot 10^{-4}$ to $2.45 \cdot 10^{-4}$ molar. $1.5 \cdot 10^{-4}$ to $6.0 \cdot 10^{-4}$

[2] Thorium $4.83 \cdot 10^{-5}$ to $9.66 \cdot 10^{-5}$ molar. $4.5 \cdot 10^{-5}$ to $1.8 \cdot 10^{-4}$

TABLE VI

SPECTROPHOTOMETRIC ESTIMATION OF THORIUM AS OXINATE

Test solution	Transmission at 320 mμ in 0.1N HCl	Density	Corresponding amount of ThO_2 mg	Diff. in mg
I 0.025 mg of ThO_2 per ml	8.9	1.051	0.0245	—0.0005
II 0.0125 mg of ThO_2 per ml	31.6	0.500	0.0120	—0.0005
Monazite 0.0103 mg of ThO_2 per ml	37.6	0.425	0.0100	—0.0003
Test solution	Transmission at 330 mμ in acetone		Corresponding amount of ThO_2 mg	Diff. in mg
I 0.025 mg of ThO_2 per ml	17.8	0.750	0.0245	—0.0005
II 0.0125 mg of ThO_2 per ml	44.7	0.350	0.01244	—0.00006
Monazite 0.0103 mg of ThO_2 per ml	52.5	0.2799	0.0100	—0.0003

The oxinates of thorium and some cerite earths

From a study of the precipitation of oxinates of Th, Ce, La in relation to pH, a pH condition for the effective separation of lanthanum from thorium has been established. It has been shown that thorium in monazite can be completely precipitated from other rare earths with oxine at pH 3.9. From a spectrochemical study of the oxinates of thorium in dilute HCl and acetone it has been concluded that the red complex with the composition $Th(C_9H_6ON)_5$ is a definite compound and not a molecular addition compound $Th(C_9H_6ON)_4,C_9H_7ON$ as has been assumed. Procedures for the colorimetric estimation of Th with oxine at wave length 320 mμ in dilute HCl and 330 mμ in acetone have also been described. It is possible to estimate as little as 2 p.p.m. of the oxide.

SUMMARY

The pH of precipitation of oxinates of thorium, cerium and lanthanum has been studied. By controlling the pH of precipitation, thorium has been separated as the oxinate.

From a spectrochemical study of the 4 and 5 oxinates of thorium in dilute hydrochloric acid, acetone, carbontetrachloride, chloroform, and toluene, it has been suggested that the 5 complex is a definite compound, but not an addition body of the 4 compound.

A colorimetric estimation of thorium has been suggested by measuring absorption at 320 mμ in hydrochloric acid and 330 mμ in acetone. 2 p.p.m. of the oxide has thus been estimated.

RÉSUMÉ

Les auteurs ont déterminé le pH de précipitation des oxinates de thorium, de cérium et de lanthane. En contrôlant le pH de précipitation, on peut séparer le thorium sous forme d'oxinate. Après une étude spectrochimique des complexes du thorium ($Th(C_9H_6ON)_4$, C_9H_7ON et $Th(C_9H_6ON)_5$) en solution dans l'acide chlorhydrique dilué, dans l'acétone, dans le tétrachlorure de carbone, dans le chloroforme et dans le toluène, les auteurs arrivent à la conclusion que le complexe étudié répond bien à la formule $Th(C_9H_6ON)_5$. Un dosage colorimétrique du thorium est proposé par mesure de l'absorption dans l'acide chlorhydrique à 320 mμ et dans l'acétoen à 330 mμ. Par ce procédé, on peut évaluer 2 p.p.m. d'oxyde de thorium.

ZUSAMMENFASSUNG

Die Autoren haben die Niederschlags-pH der Oxinate von Thor, Cer und Lanthan untersucht. Durch Kontrolle der Niederschlags-pH kann man das Thor als Oxinat abscheiden. Durch eine spektrochemische Untersuchung der Komplexe des Thors Th $(C_9H_6ON)_4$, C_9H_7ON und $Th(C_9H_6ON)_5$ gelöst in verdünnter Salzsäure, in Aceton, in Tetrachlorohlenstoff, in Chloroform und in Toluol kommen die Autoren zum Schlusse, dass der untersuchte Komplex der Formel $Th(C_9H_6ON)_5$ entspricht. Es wird eine kolorimetrische Bestimmung von Thor vorgeschlagen, welche auf der Messung der Absorption in Salzsäure bei 320 mμ und in Aceton bei 330 mμ beruht. Mit Hilfe dieser Methode können 2 p.p.m. Thoroxyd bestimmt werden.

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COLORIMETRIC DETERMINATION OF IRON IN TITANIUM ALLOYS

by

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INTRODUCTION

Iron is one of the most common elements present in titanium alloys, therefore its determination is a matter of importance. Methods have been described[4,17,18] for the determination of iron in titanium metal by the use of thiocyanate. A disadvantage of the use of thiocyanate for the colorimetric determination of iron is the instability of the color[14,18]. It was decided, therefore, to develop a method for the colorimetric determination of iron in titanium alloys using *o*-phenanthroline.

o-Phenanthroline has been used for the colorimetric determination of iron in aluminum alloys[1,11,13], copper base alloy[7], iron ores[10], red phosphorus[3], fruit products[15], eggs[2], and foods and biological materials[5,9]. None of these methods are directly applicable to the determination of iron in titanium alloys. In developing a direct procedure applicable to titanium alloys it was found that considerable time was saved by making use of the fact that hydroxylamine will oxidize titanium from the titanous to the titanic state while at the same time keeping iron in the ferrous condition. The addition of ammonium tartrate was found necessary to prevent the precipitation of titanium. Before developing the *o*-phenanthroline color, the pH of the solution was adjusted by the addition of sodium acetate solution. The effect of varying amounts of sodium acetate on the pH of the solution and the transmittance of the solution is shown in Table I. Twenty-five ml of sodium acetate solution (10 per cent.) was chosen as optimum. The pH of the solution when this amount of sodium acetate was present was 4.55. The effect of adding varying amounts of *o*-phenanthroline is shown in Table II. The use of 10 ml of *o*-phenanthroline solution (0.2 per cent.) is recommended.

A study was made of the possible interference with this direct procedure of elements that might be found in titanium alloys. The amounts of the elements that did not interfere in the determination of up to 0.75 per cent. iron are shown

TABLE I

EFFECT OF AMOUNT OF SODIUM ACETATE
(0.2 mg of iron and 0.05 gram of titanium present)

ml sodium acetate solution (10%)	pH of solution	Transmittance
0	1.50	86.2
5	1.90	34.1
10	3.28	28.9
15	4.10	28.7
20	4.38	28.2
25	4.55	28.2
30	4.54	28.3
35	4.79	28.8
40	4.90	28.5
45	4.86	28.9

TABLE II

EFFECT OF AMOUNT OF *o*-PHENANTHROLINE
(0.3 mg of iron and 0.05 gram of titanium present)

ml of *o*-phenanthroline solution (0.2%)	Transmittance
1	32.0
2	17.6
5	17.1
8	17.2
10	16.9
15	16.9

in Table III. More than 2.0 per cent. chromium caused high results because of the formation of a greenish-blue color. More than 1.6 per cent. molybdenum or 0.9 per cent. vanadium interfered because of the formation of yellow colors. More than 1.2 per cent. nickel interfered by repressing the development of the iron color. More than 1.0 per cent. cobalt interfered in two ways. It repressed the formation of the iron color and gave a yellow color with the reagent. More than 1.6 per cent. copper interfered by inhibiting the formation of the iron color and giving a yellow precipitate. If more than 1 per cent. tungsten were present, tungstic acid precipitated on the addition of the sodium acetate. The interferences described above are somewhat different from those described by FORTUNE AND MELLON[6,16]. The latter authors, however, did not have tartrate present.

TABLE III

AMOUNT OF THE ELEMENTS THAT DID NOT INTERFERE WITH THE DIRECT METHOD FOR IRON IN TITANIUM ALLOYS

Element	Added as	Amount that did not interfere (%)
Chromium	$Cr_2(SO_4)_3$	2.0[a]
Molybdenum	$(NH_4)_6Mo_7O_{24}.6H_2O$	1.6[a]
Vanadium	$(VO)_2Cl_4$	0.9[a]
Nickel	$NiCl_2.6H_2O$	1.2[a]
Cobalt	$CoCl_2.6H_2O$	1.0[a]
Copper	$CuSO_4.5H_2O$	1.6[a]
Tungsten	$Na_2WO_4.2H_2O$	1.0[a]
Manganese	$MnSO_4.H_2O$	10.0
Aluminum	$Al_2(SO_4)_3.18H_2O$	5.0
Silicon	$Na_2SiO_3.9H_2O$	5.0
Tin	$SnCl_2.2H_2O$	5.0
Calcium	$CaCl_2.2H_2O$	5.0
Magnesium	$MgSO_4.7H_2O$	5.0
Phosphorus	$(NH_4)_2HPO_4$	1.0
Boron	H_3BO_3	1.0

[a] Maximum amount permissible

The above limits of interferences apply only when up to 0.75 per cent. iron is present. For this amount of iron a 25 ml aliquot is taken. When more than 0.75 per cent. iron is present, a smaller aliquot (10 ml or less) is taken; consequently, the permissible limit of interferences is much increased. For instance, alloys containing several per cent. iron and several per cent. chromium, or several per cent. iron and several per cent. molybdenum, are readily handled by the direct method.

For alloys containing smaller amounts of iron and large amounts of chromium, tungsten, vanadium, copper, nickel, and cobalt, an ether extraction is made to separate the iron prior to its colorimetric determination. For alloys containing smaller amounts of iron and large amounts of molybdenum, the iron and molybdenum are first extracted with ether, and one ammoniacal precipitation made to separate the iron from the bulk of the molybdenum.

In the ether extraction method the sample is dissolved in hydrochloric acid, and the titanium and iron oxidized with bromine. The solution is then boiled several minutes to drive off the excess bromine and yield a constant boiling hydrochloric acid mixture. The acidity of the latter (sp. gr. 1.10)[12] has been recommended for extraction of iron by ether[8].

The methods proposed in this paper are recommended for the determination of 0.02 to 9 per cent. iron.

For the experimental work it was found necessary to use iodide titanium. Sponge titanium is not very homogeneous insofar as the iron content is concerned.

APPARATUS AND REAGENTS

Coleman Universaiamettlrophotometer, Model 14, with optically matched cuvettes 19 mm in dSerep .

Beckman pH meter equipped with glass and calomel electrodes.

Standard Iron Solution No. 1 (1 ml = 2.0 mg iron). Dissolve 2.0000 grams of National Bureau of Standards iron (55 c) in a mixture of 100 ml of water and 100 ml of hydrochloric acid by heating on the hot plate. Cool and dilute with water to 1 liter in a volumetric flask.

Standard Iron Solution No. 2 (1 ml = 0.2 mg iron). Pipette 100 ml of Standard Iron Solution No. 1 into a 1-liter volumetric flask, add 25 ml of hydrochloric acid and dilute to the mark with water.

Hydrochloric acid, sp. gr. 1.19.

Dilute Hydrochloric Acid (sp.gr. 1.10). Dilute 1000 ml of hydrochloric acid (sp.gr. 1.19) to 1850 ml with water.

Dilute Hydrochloric Acid (4 per cent.). Dilute 20 ml of hydrochloric acid (sp.gr. 1.19) to 500 ml with water.

Hydroxylamine Hydrochloride Solution (2 per cent.). Dissolve 10 grams of hydroxylamine hydrochloride in water and dilute to 500 ml with water.

Ammonium Tartrate Solution (10 per cent.). Dissolve 100 grams of ammonium tartrate in water and dilute to 1 liter with water.

Sodium Acetate Solution (10 per cent.). Dissolve 100 grams of sodium acetate trihydrate in water and dilute to 1 liter with water.

Ortho-Phenanthroline Solution (0.2 per cent.). Dissolve 2 grams of *o*-phenanthroline monohydrate in water and dilute to 1 liter with water.

Bromine, cp.

Ether, USP. Use a brand that is sold in glass bottles (not cans).

Nitric Acid, sp.gr. 1.41.

Ammonium Hydroxide, sp.gr. 0.90.

Dilute Ammonium Hydroxide (3 per cent.). Dilute 30 ml of ammonium hydroxide to 1 liter with water.

PROCEDURE

Preparation of calibration curve

Weigh out 1-gram samples of iodide titanium into covered 250-ml beakers and add the following aliquots of Standard Iron Solution No. 2: 5 ml, 10 ml, 15 ml, 20 ml, 30 ml, and 35 ml. Carry along a sample of iodide titanium as a blank. Add 20 ml of water and 20 ml of hydrochloric acid and warm on the hot plate until the samples have dissolved. Cool and transfer to 500-ml volumetric flasks. Dilute to the mark, shake, and pipette 25-ml aliquots into 100-ml volumetric flasks. Add 10 ml of hydroxylamine hydrochloride solution (2 per cent.), 5 ml of ammonium tartrate solution (10 per cent.), 25 ml of sodium acetate solution (10 per cent.) and 10 ml of *o*-phenanthroline solution (0.2 per cent.). Swirl after the addition of each reagent. Dilute to the mark and shake. Allow to stand 15 minutes, and read the transmittance at 490 millimicrons with a spectrophotometer. Set the spectrophotometer at 100 per cent. transmittance with the blank. Plot the per cent. transmittance against the number of milligrams of iron present in the 100-ml volumetric flasks. The calibration curve obtained by the authors is shown in Fig. 1.

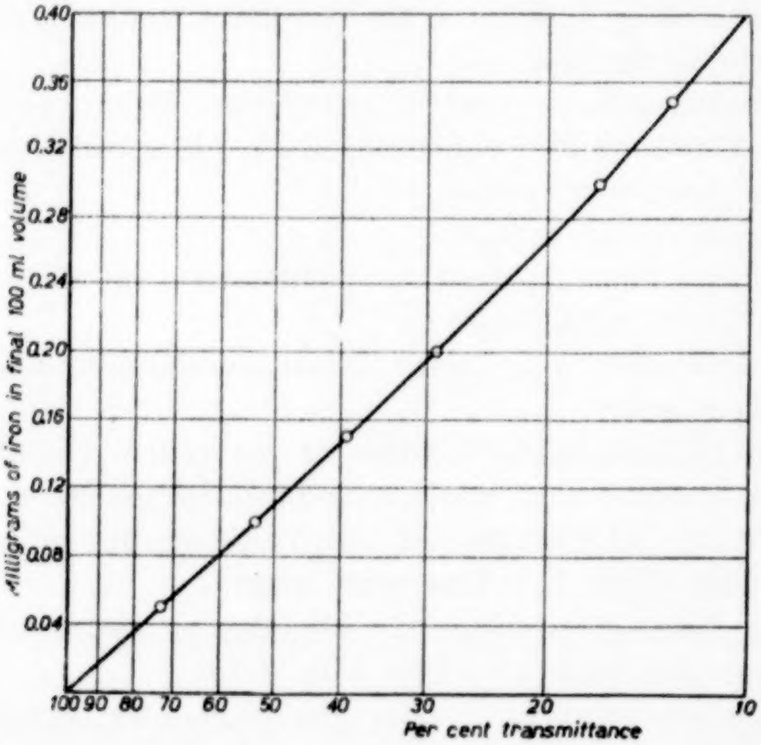

Fig. 1. Calibration curve for the colorimetric determination of iron in titanium alloys.

Direct method

Weigh out a 1-gram sample into a covered 250-ml beaker and add 20 ml of water and 20 ml of hydrochloric acid. Warm on the hot plate until the sample has dissolved. Cool, transfer to a 500-ml volumetric flask, dilute to the mark and shake. Pipette an aliquot into a 100-ml volumetric flask. For alloys containing up to 0.75 per cent. iron use a 25-ml aliquot; for alloys containing 0.75 to 1.8 per cent. iron use a 10-ml aliquot; for alloys containing 1.8 to 3.5 per cent. iron use a 5-ml aliquot; for alloys containing 3.5 to 9 per cent. iron use a 2-ml aliquot. If an aliquot of less than 25 ml is taken, bring the volume up to 25 ml by the addition of dilute hydrochloric acid (4 per cent.) Add 10 ml of hydroxylamine hydrochloride solution (2 per cent.), 5 ml of ammonium tartrate solution (10 per cent.), 25 ml of sodium acetate solution (10 per cent.), and 10 ml of *o*-phenanthroline solution (0.2 per cent.). Swirl after the addition of each reagent. Dilute to the mark, and shake. Allow to stand 15 minutes and read the transmittance at 490 millimicrons with a spectrophotometer. Set the spectrophotometer at 100 per cent. transmittance with the blank prepared by adding the reagents to 25 ml of dilute hydrochloric acid (4 per cent.). Convert the readings to mg of iron by consulting the calibration curve. Find the per cent. iron present in the sample by use of the following formulas:

If a 25-ml aliquot were taken
% Iron = mg of iron as read from curve × 2
If a 10-ml aliquot were taken
% Iron = mg of iron as read from curve × 5
If a 5-ml aliquot were taken
% Iron = mg of iron as read from curve × 10
If a 2-ml aliquot were taken
% Iron = mg of iron as read from curve × 25.

Ether extraction method

Weigh a 1-gram sample into a covered 250-ml beaker and add 10 ml of water and 30 ml of hydrochloric acid. Warm on the hot plate until the sample is dissolved. Cool to room temperature and add bromine a little at a time until the blue titanous color disappears. Cover with a watch glass, heat to boiling and boil 10 minutes. Add 40 ml of dilute hydrochloric acid (sp.gr. 1.10) and cool to about 10° C in an ice bath. Transfer to a 250-ml separatory funnel and wash the beaker with a little dilute hydrochloric acid (sp.gr. 1.10). Add 50 ml of ether, shake for about a half minute and allow the layers to separate. Drain the bottom aqueous layer into the original 250-ml beaker. Pour the ether layer through the top of the funnel into a clean 250-ml beaker. Extract 4 more times using 30 ml portions of ether. Evaporate the combined ether extracts to dryness by heating on a steam bath. Add 15 ml of water and 15 ml of hydrochloric acid. Heat to boiling and boil for a few minutes. Cool to room temperature and transfer to a 500-ml volumetric flask. Dilute to the mark and determine the iron colorimetrically as described under the direct method.

If a large amount of molybdenum is present, extract with ether and evaporate to dryness as described above. Add 15 ml of water, 15 ml of hydrochloric acid and 2 ml of nitric acid (to ensure that the iron is in the oxidized state). Heat to boiling and boil for a few minutes. Dilute to about 100 ml with water. Make alkaline to litmus paper with ammonium hydroxide and add a few ml excess ammonium hydroxide. Heat to boiling and boil for a minute. Filter through a medium texture filter paper (Whatman No. 40), and wash the beaker and filter paper with hot dilute ammonium hydroxide solution (3 per cent.). Dissolve the precipitate back into the original 250-ml beaker with a mixture of equal parts of hydrochloric acid and water that has been heated almost to boiling. Wash the filter paper with hot water. Cool the filtrate to room temperature and transfer to a 500-ml volumetric flask. Dilute to the mark and determine the iron colorimetrically as described under the direct method.

RESULTS

The results obtained for iron by the direct method using synthetic alloys are shown in Table IV. The results obtained for iron by the ether extraction method using synthetic alloys are shown in Table V.

TABLE IV

RESULTS FOR IRON IN SYNTHETIC TITANIUM ALLOYS BY DIRECT METHOD

Iron present (%)	Average iron found (%)	Std dev. (%)	No. of determinations
0.020	0.019	0.002	5
0.050	0.050	0.003	5
0.100	0.101	0.003	5
0.400	0.400	0.004	5
0.600	0.604	0.006	5
1.00	1.01	0.016	5
3.00	2.99	0.034	5
5.00	5.02	0.070	5
9.00	9.03	0.129	5

TABLE V

RESULTS FOR IRON IN SYNTHETIC TITANIUM ALLOYS BY ETHER EXTRACTION METHOD

Iron present (%)	Other elements present (%)	Iron found (%)
0.100	10 Chromium	0.102
0.400	,,	0.398
0.600	,,	0.604
0.100	10 Tungsten	0.102
0.400	,,	0.404
0.600	,,	0.594
0.100	10 Vanadium	0.100
0.400	,,	0.402
0.100	10 Copper	0.104
0.400	,,	0.396
0.100	10 Nickel	0.098
0.400	,,	0.398
0.100	10 Cobalt	0.100
0.400	,,	0.402
0.100	10 Molybdenum	0.098
0.400	,,	0.398
0.600	,,	0.604

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SUMMARY

There is need for an improved method for the determination of iron in titanium alloys. In this paper a colorimetric method using *o*-phenanthroline is proposed. The method is applicable to the range of 0.02 to 9 per cent. iron. Two modifications of a basic procedure are described. One modification, applicable to ordinary titanium alloys, is a direct method. A second modification, applicable to alloys containing large amounts of certain alloying elements, calls for a prior separation of the iron by an ether extraction. In a direct method a one gram sample is dissolved in hydrochloric acid and an aliquot of the solution taken. Hydroxylamine and ammonium tartrate are added, the pH of the solution is adjusted by the addition of sodium acetate, and *o*-phenanthroline added. A study was made to find the best pH and optimum amount of *o*-phenanthroline for the development of the color.

RÉSUMÉ

Les auteurs proposent une méthode colorimétrique pour le dosage du fer dans les alliages de titane, au moyen d'*o*-phénanthroline. Ce procédé permet de doser 0.02 à 9% de fer. Deux modifications sont décrites:

1) une méthode directe applicable aux alliages de titane ordinaires;

2) une méthode applicable aux alliages renfermant de grandes quantités d'éléments étrangers; on effectue une séparation préalable du fer par extraction à l'éther.

Dans la méthode directe, un gramme de l'échantillon est dissous dans l'acide chlorhydrique. On prélève une partie aliquote de la solution. On ajoute de l'hydroxylamine et du tartrate d'ammonium; on tamponne la solution par l'acétate de sodium et on ajoute l'*o*-phénanthroline.

Une étude a été effectuée pour déterminer le meilleur pH et la quantité optimum d'*o*-phénanthroline nécessaire au développement de la coloration.

ZUSAMMENFASSUNG

Die Autoren schlagen eine Methode vor zur kolorimetrischen Bestimmung von Eisen in Titanlegierungen mit Hilfe von *o*-Phenanthrolin. Diese Methode ermöglicht eine Bestimmung von 0.02 bis 9% Eisen. Zwei Modifikationen wurden beschrieben:

1) eine direkte Bestimmung, welche auf die gewöhnlichen Titanlegierungen anwendbar ist;

2) eine Methode, welche auf die Legierungen anwendbar ist, die grössere Quantitäten von fremden Elementen enthalten. Es wird vorgängig eine Abtrennung des Eisens durch eine Ätherextraktion vorgenommen.

Bei der direkten Methode wird ein Gramm der Probe in Salzsäure aufgelöst. Man entnimmt einen bestimmten Teil der Lösung. Man gibt Hydroxylamin und Ammoniumtartrat hinzu; die Lösung wird mit Natriumacetat gepuffert und nun gibt man das *o*-Phenanthrolin hinzu.

Das beste pH wurde festgelegt und die optimale Quantität von *o*-Phenanthrolin, welche zur Entwicklung der Farbe notwendig ist.

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DIRECT COLORIMETRIC DETERMINATION OF SMALL AMOUNTS OF TUNGSTEN IN TITANIUM

by

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INTRODUCTION

One of the pressing analytical problems facing the titanium industry is the development of a rapid and accurate method for the determination of small amounts of tungsten in titanium. Tungsten electrodes are used in melting titanium; consequently, as much as 0.1 per cent. tungsten is sometimes introduced during the casting process. The effect of this amount of tungsten on titanium has been subject to considerable debate. One reason for the uncertainty about the matter is the lack of a rapid and accurate method for determining small amounts of tungsten in titanium. A satisfactory method for the determination of tungsten in titanium, as shown by an interlaboratory study[4], is the gravimetric benzoin oxime method of CODELL[2]. However, this method, like gravimetric methods in general, is not readily applicable to the determination of very small amounts of tungsten. Ordinarily, the spectrograph is very useful in determining small amounts of metals. However, because of the insensitivity of the tungsten lines, the spectrograph has proved only of limited value for the determination of tungsten in titanium.

SHORT[3] has proposed a method for the determination of tungsten in titanium in which the green toluene dithiol complex is extracted with amyl acetate. The conditions for this determination were found to be somewhat critical[4]. BACON[1] has described a method for determining tungsten in titanium by means of the yellow thiocyanate color. In this method stannous chloride is added to reduce the tungsten before the addition of the thiocyanate. Many operators in different laboratories have had difficulty with the method[4]. Therefore, an investigation was conducted to find the reasons for the shortcomings of the procedure. It was found that one reason why erratic results were obtained was that titanium in the quadrivalent state (but not the trivalent state) gives a yellow color with thiocyanate. On the addition of stannous chloride in BACON's method most, but not all, of the titanium is reduced to the trivalent state. Another error in BACON's method is the formation of hydrogen sulfide by the reaction of stannous chloride with the thiocyanate. This hydrogen sulfide caused fading of the color. It was reasoned that these two errors could be eliminated by the use of a reducing agent that would reduce the tungsten and all the titanium, and yet would readily be destroyed so as not to react with the thiocyanate. After trying many reducing agents, it was found that metallic zinc admirably satisfied all of these requirements. The method as finally developed was extremely rapid and very accurate. It was applicable to the determination of 0.005 to 0.3 per cent. tungsten in titanium.

APPARATUS AND REAGENTS

Coleman Universal Spectrophotometer Model 14, with optically matched 13 × 13 × 105 mm cuvettes.

Standard Tungsten Solution. Dissolve 0.3588 gram of sodium tungstate, $Na_2WO_4.2H_2O$, in water and dilute to 2 liters with water in a volumetric flask. One ml of this solution contains 0.10 mg tungsten. One ml of the solution is equivalent to 0.05 per cent. tungsten on a 0.2 gram sample.

Potassium Thiocyanate Solution (5 per cent.). Dissolve 25 grams of potassium thiocyanate, KCNS, in water and dilute to 500 ml with water.

Hydrochloric Acid, sp. gr. 1.19.

Granulated Zinc, cp, 20 mesh.

RECOMMENDED METHOD

Preparation of calibration curve

Weigh 0.2 gram portions of titanium sponge metal into covered 250 ml beakers and add 0.4, 1, 2, 3, 4, 5 and 6 ml portions of standard tungsten solution measured with an accurate micro-burette. Add 5 ml of water and 25 ml of hydrochloric acid and warm gently on the hot plate until the titanium has dissolved. As soon as the samples are in solution, cool the beakers to room temperature in a running water bath. Transfer the solutions to 50 ml volumetric flasks which contain 0.7 gram of granulated zinc (20 mesh). As soon as the reaction has ceased, place stoppers on the volumetric flasks. Add 10 ml of potassium thiocyanate solution (5 per cent.) measured with a pipette, and place the volumetric flasks in a running water bath for 15 minutes. Dilute to the mark, shake andmeasurethetransmittance at 410 millimicrons with a spectrophotometer. Set the spectrophotometer at 100 per cent transmittance with a blank solution obtained by carrying 0.2 gram of titanium sponge metal through the entire procedure. Plot the per cent. tungsten against the per cent. transmittance. The calibration curve obtained by the authors is shown in Fig. 1.

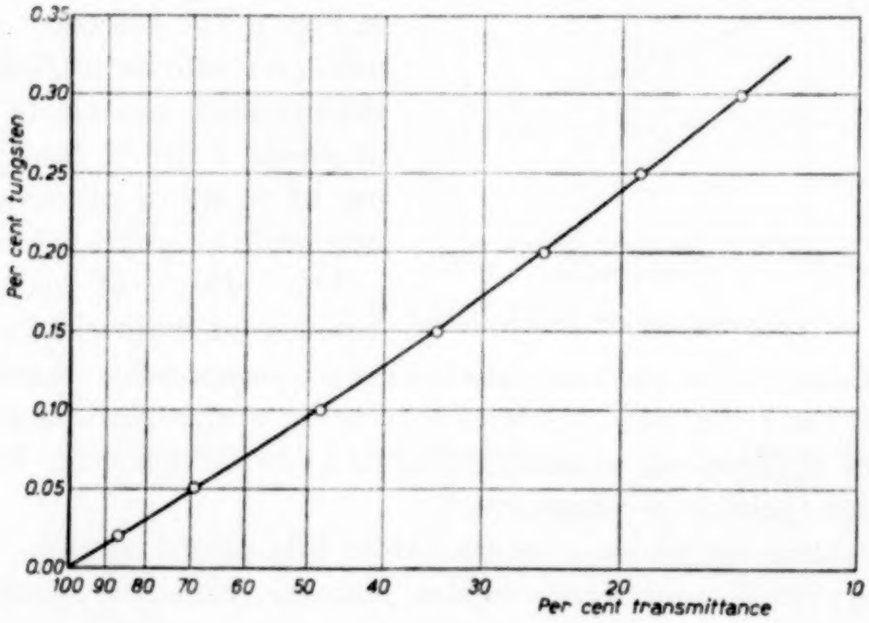

Fig. 1. Calibration curve for the colorimetric determination of tungsten in titanium by thiocyanate.

Procedure

Weigh a 0.2 gram sample into a covered 250 ml beaker and add 5 ml of water and 25 ml of hydrochloric acid. Warm gently on the hot plate until the sample has dissolved and then proceed as described under preparation of calibration curve. Convert the spectrophotometer reading to per cent. tungsten by consulting the calibration curve.

EXPERIMENTAL

At first, attempts were made to read the tungsten thiocyanate color near the ultraviolet region at 350 millimicrons in order to eliminate the effect of the blue titanous ion. However, erratic results and high blanks were obtained at this wave length, probably due to polymerization of the thiocyanate. It was found that excellent results were obtained at 410 millimicrons; consequently, all subsequent readings were made at this wave length.

The effect of using different amounts of titanium (in the absence of tungsten) is shown in Fig. 2. It is seen that a variation of 5 per cent. in the titanium content

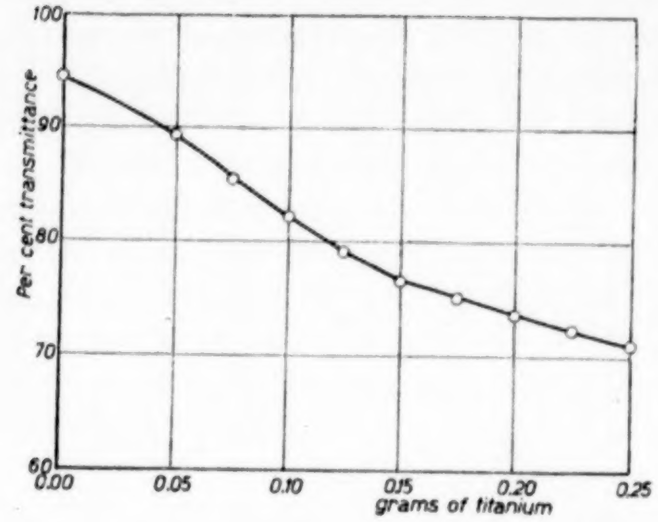

Fig. 2. Effect of amount of titanium.

of the metal causes no appreciable error.

The effect of adding different amounts of thiocyanate (in the presence of 0.30 mg of tungsten) is shown in Fig. 3. The intensity of the color increases with increasing amounts of thiocyanate, but starts to level off at about 8 ml of thiocyanate. The use of 10 ml of thiocyanate measured with a pipette is recommended.

The effect of using different amounts of hydrochloric acid in dissolving the sample (in the presence of 0.30 mg of tungsten) is shown in Fig. 4. The intensity of the color increases with increasing hydrochloric acid concentration, but starts to level off at about 20 ml of hydrochloric acid. The use of 25 ml of hydrochloric acid is recommended.

The color is stable for about 2 hours. After this period of time the readings obtained for very small amounts of tungsten increase, while the readings obtained for larger amounts of tungsten decrease.

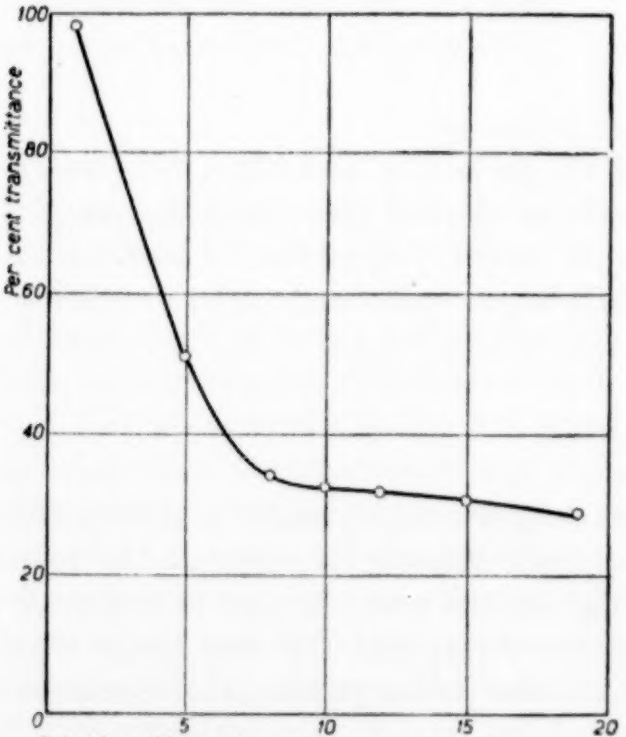

Fig. 3. Effect of amount of thiocyanate.

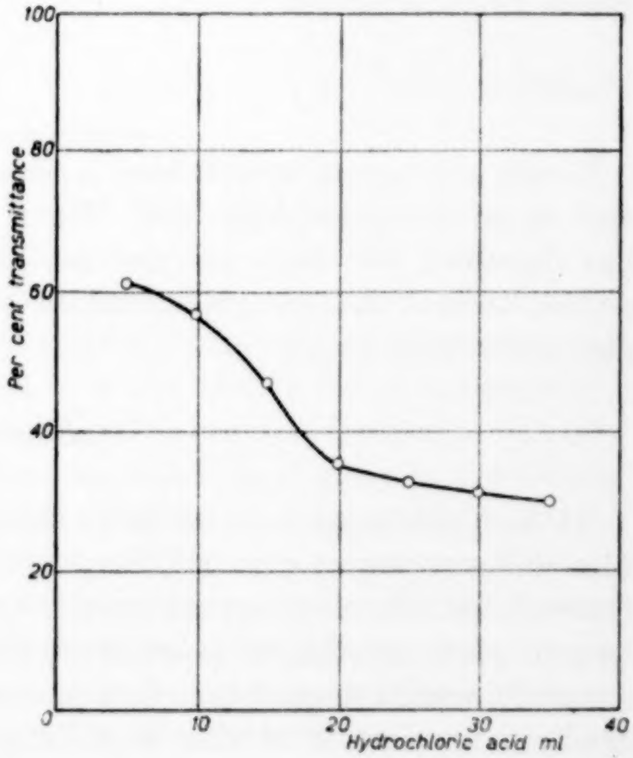

Fig. 4. Effect of amount of hydrochloric acid used to dissolve sample.

TABLE I

RESULTS FOR TUNGSTEN IN SYNTHETIC SAMPLES

Tungsten added (%)	Tungsten found (%)	Std dev. (%)	No. of determinations
0.005	0.005	0.001	5
0.020	0.019	0.002	5
0.050	0.050	0.002	5
0.150	0.151	0.003	5
0.300	0.298	0.005	5

TABLE II

RESULTS FOR TUNGSTEN IN THE PRESENCE OF POSSIBLE INTERFERENCES

Element added	Amount added (%)	Added As	Tungsten added (%)	Tungsten found (%)
Molybdenum	0.05	$(NH_4)_6Mo_7O_{24}.4H_2O$	0.000	0.004
,,	0.15	,,	,,	0.010
,,	0.25	,,	,,	0.022
,,	0.75	,,	,,	0.040
,,	1.00	,,	,,	0.055
,,	0.05	,,	0.150	0.154
,,	0.15	,,	,,	0.156
,,	0.25	,,	,,	0.164
,,	0.75	,,	,,	0.195
,,	1.00	,,	,,	0.208
Vanadium	0.05	$(VO)_2Cl_4$	0.000	0.004
,,	0.25	,,	,,	0.016
,,	0.75	,,	,,	0.044
,,	1.00	,,	,,	0.052
,,	0.05	,,	0.150	0.154
,,	0.25	,,	,,	0.157
,,	0.75	,,	,,	0.176
,,	1.00	,,	,,	0.190
Chromium	0.5	$Na_2Cr_2O_7.2H_2O$[a]	0.000	0.003
,,	1.0	,,	,,	0.006
,,	2.5	,,	,,	0.017
,,	5.0	,,	,,	0.029
,,	0.5	,,	0.150	0.153
,,	1.0	,,	,,	0.158
,,	2.5	,,	,,	0.168
,,	5.0	,,	,,	0.175

[a] The chromate is reduced to a lower valence state when the sample is dissolved.

TABLE II

RESULTS FOR TUNGSTEN IN THE PRESENCE OF POSSIBLE INTERFERENCES

Element added	Amount added (%)	Added as	Tungsten added (%)	Tungsten found (%)
Copper	0.25	$CuSO_4{\cdot}5H_2O$	0.000	0.002
,,	1.0	,,	,,	0.006
,,	0.25	,,	0.150	0.153
,,	1.0	,,	,,	0.082
Nickel	5.0	$NiCl_2{\cdot}6H_2O$	0.000	0.006
,,	,,	,,	0.150	0.154
Cobalt	5.0	$CoCl_2{\cdot}6H_2O$	0.000	0.003
,,	,,	,,	0.150	0.154
Iron	5.0	$FeCl_3{\cdot}6H_2O$	0.000	0.000
,,	,,	,,	0.150	0.152
Manganese	5.0	$MnSO_4{\cdot}H_2O$	0.000	0.000
,,	,,	,,	0.150	0.152
Silicon	5.0	$Na_2SiO_3{\cdot}9H_2O$	0.000	0.001
,,	,,	,,	0.150	0.148
Phosphorus	1.0	$(NH_4)_2HPO_4$	0.000	0.000
,,	,,	,,	0.150	0.149
Boron	1.0	H_3BO_3	0.000	0.001
,,	,,	,,	0.150	0.153
Tin	2.5	$SnCl_2{\cdot}2H_2O$	0.000	0.000
,,	,,	,,	0.150	0.152
Aluminum	5.0	$Al_2(SO_4)_3{\cdot}18H_2O$	0.150	0.148
Calcium	5.0	$CaCl_2{\cdot}2H_2O$	0.150	0.149
Magnesium	5.0	$MgSO_4{\cdot}7H^2O$	0.150	0.149

RESULTS AND INTERFERENCES

The results obtained for synthetic samples prepared by adding standard tungsten solution to 0.2 gram samples of sponge titanium are shown in Table I.

The results obtained in the presence of possible interfering elements are shown in Table II. The method is designed for titanium metal containing only moderate amounts of impurities, rather than for titanium alloys. However, because of the interest in the possible application of the method to titanium alloys a complete investigation was made of the effect of interferences. Molybdenum gives an interfering thiocyanate color. When less than 0.25 per cent. molybdenum is present, the intensity of the molybdenum color is roughly one-tenth the intensity of the tungsten color. As the per cent. of molybdenum increases, the intensity of the molybdenum color as compared to the tungsten color decreases. Vanadium gives

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an interfering color that is somewhat less sensitive than the molybdenum color. However, the interference from vanadium is erratic. The interference decreases as the amount of tungsten in the sample increases. Chromium is reduced by the zinc to blue chromous ion which shows some absorption at 410 millimicrons. The interference from chromium is readily corrected for, every one per cent. chromium being equivalent to about 0.006 per cent. tungsten. More than 0.2 per cent. copper should not be present because of the precipitation of cuprous thiocyanate. This precipitation of the cuprous thiocyanate can cause high or low results. There is a tendency toward high results because of the turbidity, and a tendency toward low results because the thiocyanate is used up for the precipitation of the cuprous thiocyanate rather than development of the tungsten thiocyanate color. Nickel and cobalt show a very slight interference due to the color of their salts. This interference could be readily corrected for. For alloys containing less than 2 per cent. nickel or cobalt it could be disregarded.

SUMMARY

There is need for a rapid and accurate method for the determination of small amounts of tungsten in titanium. In this paper a direct colorimetric method is proposed for the determination of tungsten in titanium that is applicable to the range of 0.005 to 0.3 per cent. tungsten. The sample is dissolved in hydrochloric acid and the titanium and tungsten reduced with metallic zinc. Thiocyanate is added and the yellow color read at 410 millimicrons with a spectrophotometer. A study was made of the best conditions for developing the color, including the effect of varying amounts of titanium, thiocyanate and hydrochloric acid. An investigation was made to determine the proper wave length for reading the color, the stability of the color and effect of interferences.

RÉSUMÉ

Une méthode rapide et précise pour le dosage de faibles teneurs de tungstène dans le titane faisant défaut, les auteurs ont mis au point un procédé permettant de doser 0.005 à 0.3% de tungstène. L'échantillon à analyser est dissous dans l'acide chlorhydrique. Le titane et le tungstène sont réduits par le zinc métallique. On ajoute le thiocyanate; l'intensité de la coloration jaune est mesurée au spectrophotomètre à 410 mμ. Les meilleures conditions pour le développement de la coloration ont été étudiées, de même que l'effet de différentes concentrations en titane, thiocyanate et acide chlorhydrique. On a déterminé également la longueur d'onde propre à ce dosage, la stabilité de la coloration et l'effet des interférences.

ZUSAMMENFASSUNG

Da eine schnelle und präzise Methode für die Bestimmung von kleinen Quantitäten von Wolfram in Titan fehlt, haben die Autoren ein Verfahren ausgearbeitet, welches eine quantitative Bestimmung von 0.005 bis 0.3% Wolfram gestattet. Die zu untersuchende Probe wird in Salzsäure aufgelöst. Das Titan und das Wolfram werden durch metallisches Zink reduziert. Man gibt das Rhodanid hinzu; die Intensität der gelben Färbung wird mit dem Spektrophotometer bei 410 mμ gemessen. Es wurden die besten Bedingungen für die Entwicklung der Farbe festgelegt. Desgleichen der Einfluss von verschiedenen Konzentrationen von Titan, von Rhodanid und von Salzsäure. Man hat auch die für diese Bestimmung zu benützende Wellenlänge bestimmt sowie die Stabilität der Färbung und der Einfluss der Interferenz.

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EINE NEUE PHOTOMETRISCHE BESTIMMUNG FÜR NICKEL MIT AETHYLENDIAMINTETRAESSIGSÄURE

von

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EINLEITUNG

Die bisher übliche photometrische Nickelbestimmung beruht auf der Fällung des Nickels mit Dimethylglyoxim. Nach der älteren photometrischen Methode wird das gebildete Nickeldimethylglyoxim durch Oxydationsmittel[8] in eine gefärbte photometrierbare Verbindung überführt. Wie vor kurzem gezeigt werden konnte[1] lässt sich vorteilhafter Nickel nach Fällung mit Dimethylglyoxim durch Ausschütteln[10] mit Chloroform nach kurzem Trocknen, direkt photometrieren. Obwohl dieses Verfahren einen erheblichen Fortschritt bedeutet, ist es aufgrund seiner hohen Empfindlichkeit wenig bequem, bei Vorliegen hoher Nickelgehalte. Bekanntlich reicht die Messgenauigkeit moderner Filterphotometer z.B. Elko II aus, um auch hohe Legierungsanteile in Metall-Legierungen photometrisch bestimmen zu können[2]. Man ist nämlich gezwungen bei Anwendung des Dimethylglyoxim-Bestimmungsverfahrens relativ hohe Verdünnungen anzuwenden. Bessere Möglichkeiten ergeben sich bei der Anwendung der Nitrilotriessigsäure[3,4,9] oder Äthylendiamintetraessigsäure[5,6,7]. Da sich diese Verfahren in der Betriebsschnellanalyse sehr gut bewährt haben, sollen in dem nachfolgenden die Grundlagen der neuen photometrischen Bestimmungsmethode mit Äthylendiamintetraessigsäure kurz beschrieben werden, nachdem wir schon über einige andere Möglichkeiten früher berichtet haben[5,6,7].

VERSUCHE UND VERSUCHSERGEBNISSE

Alle bei den nachfolgend beschriebenen Versuchen benutzten Reagenzien, waren soweit eine Abweichung nicht angegeben ist Präparate pro Analysi der Firma Merck, Darmstadt bezw. der chemischen Fabrik vormals Siegfried, Zofingen (Schweiz) oder Riedel de Haen Seelze. Das Nickel wurde in Form einer sehr reinen Spezial-Qualität Karbonylnickel benutzt.

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Apparatur

Die optischen Messungen zur Ermittlung der Durchlässigkeitskurven der Nickelkomplexverbindung der Äthylendiamintetraessigsäure wurde mit einem Spektralphotometer mit Monochromator Type M4 der Firma Carl Zeiss, Oberkochen ausgeführt. Die weiteren Untersuchungen wurden mit Hilfe filterphotometrischer Messungen (Substitutionsmethode) im Gerät Elko II der Firma Carl Zeiss Oberkochen durchgeführt. Das Gerät Elko II wurde hierbei mit der Glühlampe, Filter S57E und verschiedenen Küvetten benutzt. Im übrigen kam bei der Benutzung dieses Gerätes die schon früher ausführlich beschriebene Arbeitstechnik zur Anwendung[5,6,7,11].

Die verwendeten Volumenmessgeräte waren amtlich geeicht und wurden sorgfältig benutzt. Ausserdem blieb die Arbeitstemperatur immer nahe bei 20° C, doch fand kein Thermostat Verwendung. Die Messung der pH-Werte wurde auf elektrometrischem Wege (Röhrenvoltmeter) durchgeführt.

Durchlässigkeitskurve des Komplexes der Äthylendiamintetraessigsäure mit Nickelsalz

Es wurden Nickelsalzlösungen (mit 50 mg Ni in 100 ml) mit überschüssigem Komplexon III versetzt und auf verschiedene pH-Werte gebracht. Diese so erhaltenen Lösungen wurden im Spektralphotometer auf ihre Lichtdurchlässigkeit in verschiedenen Spektralbereichen gemessen. Man kann aus der Abbildung 1

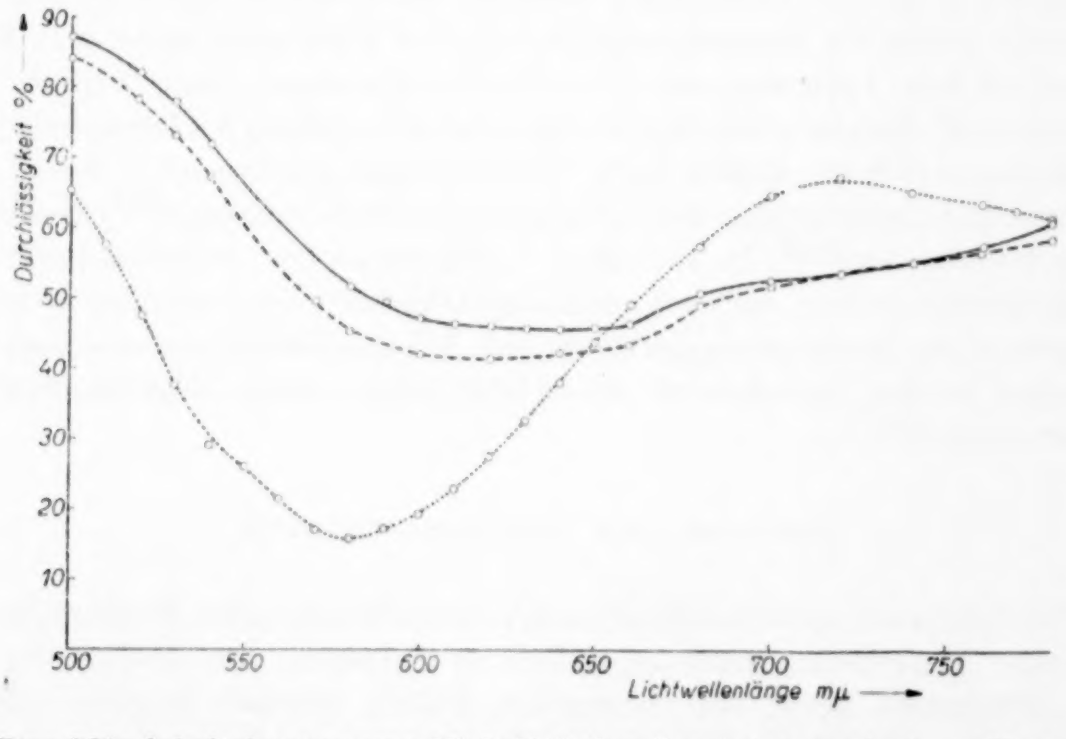

Fig. 1. Durchlässigkeitskurven von Nickeläthylendiamintetraessigsäure-Komplexen. 50 mg Ni/100 ml Lösung, 1.00 cm Küvette (aufgenommen mit Spektralphotometer M4 Carl Zeiss, Oberkochen)

—— pH = 1; - - - - - pH = 5; . . . . . pH = 11 entnehmen, dass bei den Nickelsalzlösungen mit dem pH-Wert 1 und 5 das Gebiet von 580 bis 750 mμ für eine photometrische Messung geeignet sein muss. Die Kurve der Lösung die bei einem pH-Wert von 11 unter Zusatz von Ammoniak gemessen wurde zeigt, dass der Kurvenverlauf durch eine chemische Reaktion des Ammoniaks mit dem Komplex eine wesentliche Änderung erfährt.

Auswahl der Filter für das Gerät Elko II

Da sich aufgrund der Durchlässigkeitskurven mehrere Messmöglichkeiten für eine filterphotometrische Messung ergeben, haben wir die gleiche Nickellösung mit den verschiedenen Filtern in der 5.000 cm Küvette unter Benutzung der Glühlampe gemessen. Hierbei betrug die Nickelkonzentration 2 mg Nickel pro ml Lösung. Das Ergebnis dieser Versuche ist in der Tabelle I zusammengefasst.

TABELLE I

MESSUNGEN DES NICKEL-ÄTHYLENDIAMINTETRAESSIGSÄUREKOMPLEXES MIT VERSCHIEDENEN S FILTERN

Messbedingung: Gerät Elko II mit Glühlampe in 5.000 cm Küvetten

Filter	Extinktion *berechnet* aus dem Durchlassgrad für 5.000 cm Küvetten	Durchlässigkeit in % abgelesen
S75E	0.3905	40.69
S72E	0.3835	41.35
S57E	0.6253	23.70
S55E	0.4054	39.32
S53E	0.2541	55.70
S45E	0.1267	74.70
S42E	0.4548	35.09
S38E	1.15	7.00

Für die weiteren Messungen wurde das S Filter 57E benutzt, obwohl sich mit dem Filter S38E höhere Empfindlichkeiten erhalten liessen. Es erwies sich nicht zweckmässig, mit dem Filter S38E die Ausarbeitung vorzunehmen, da bekanntlich auch das Eisen in Form seiner entsprechenden Komplexonverbindung hier sein Absorptionsmaximum aufweist[5].

Abhängigkeit der Extinktion des Nickelkomplexes der Äthylendiamintetraessigsäure von verschiedenen Salzen bei verschiedenen pH-Werten

Zu einer Nickellösung welche 88.50 mg Nickel als Nitrat und 2.5 ml Salpetersäure 1:1 enthielt wurden 20 ml Natriumacetatlösung 20% oder Ammoniumacetat 20% und wechselnde Mengen von Natronlauge oder Ammoniak zugegeben. Anschliessend wurden 20 ml Komplexonlösung (0.1 molar) hinzugefügt und der 100 ml Kolben zur Marke aufgefüllt. Der jeweilige pH-Wert der Lösung wurde elektrometrisch gemessen. Die Messung der Durchlässigkeit wurde mit Filter S57E in 5.000 cm Küvetten und der Glühlampe im Gerät Elko II durchgeführt.

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In der Abb. 2 sind die erhaltenen Messergebnisse grafisch dargestellt. Die erhaltene Kurve hat drei Aste. Der Kurvenabschnitte 1 zeigt zunächst ein schwaches Ansteigen und es ist im pH-Bereich von 5.55 bis 6.82 konstant. Es ist hierbei gleich, ob in der Analysenlösung Ammonium- oder Natriumionen vorhanden sind. Ab pH 6.82 wird ein Zwickel erhalten. Der Kurvenabschnitt 3 zeigt, dass die NH_3-Gruppe mit als farbbildendes Reagenz auftritt. Daher darf ab pH = 6.8 keine Ammoniumverbindung anwesend sein, um Störungen zu vermeiden.

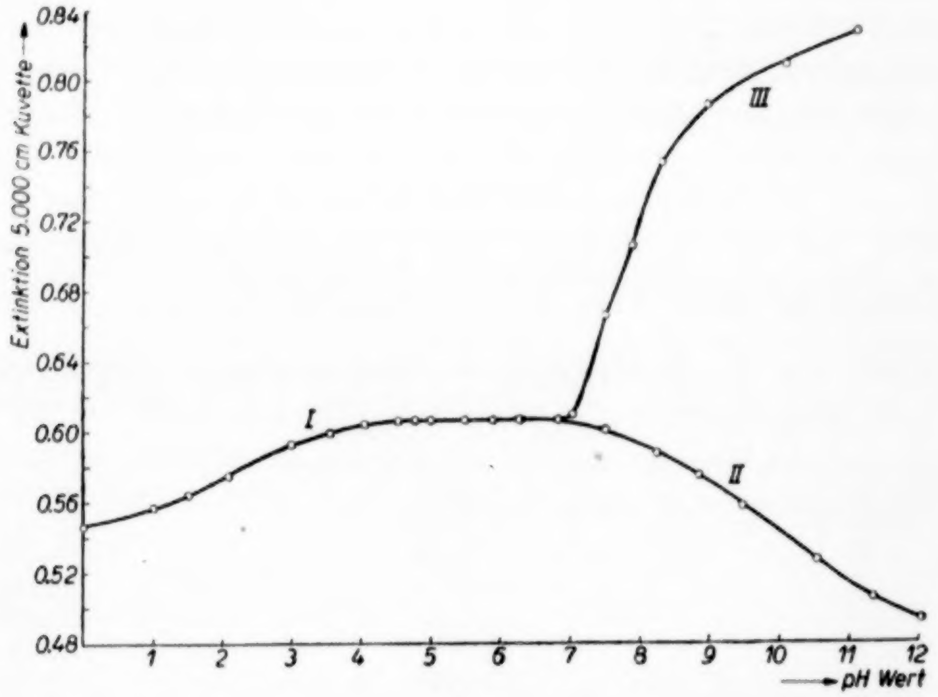

Fig. 2. Abhängigkeit der Extinktion des Nickelkomplexes der Äthylendiamintetraessigsäure von verschiedenen Puffersubstanzen bei verschiedenen pH-Werten.

Einfluss von verschiedenen Säuren auf die Extinktion des Nickelkomplexes mit Äthylendiamintetraessigsäure

Da das auszuarbeitende Bestimmungsverfahren für die Bestimmung hoher Nickelgehalte und somit als Präzisionsmethode dienen soll, musste ein etwaiger Einfluss von verschiedenen Säuren auf die Ausbildung der Färbung untersucht werden.

Versuchsführung. 9 Lösungen mit 90.0 mg, 80.0 mg und 70.0 mg Nickel davon jeweils 3 als Nickelsulfat, Nitrat und Bromid wurden mit 15 ml Natriumacetat-Lösung 20%ig und 20 ml Komplexonlösung (0.1 molar) versetzt. Die Messung erfolgte in der 5.000 cm Küvette Filter S57E und Glühlampe im Elko II. Die erhaltenen Messwerte sind in der Tabelle II zusammengefasst

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TABELLE II

EINFLUSS VON VERSCHIEDENEN SÄUREN AUF DIE EXTINKTION DES NICKELKOMPLEXES MIT ÄTHYLENDIAMINTETRAESSIGSÄURE

Messbedingung: Gerät Elko II mit Glühlampe, Filter S57E in 5.000 cm Küvetten

mg Nickel vorliegend als Nickelsalz	Durchlässigkeit in % abgelesen	Extinktion für 5.000 cm Küvetten	pH-Wert
Nickelsulfat			
90.00	24.20	0.6162	5.31
80.00	28.42	0.5464	5.30
70.00	33.31	0.4774	5.27
Nickelnitrat			
90.00	24.20	0.6162	5.30
80.00	28.42	0.5464	5.28
70.00	33.31	0.4774	5.32
Nickelchlorid			
90.00	24.21	0.6160	5.25
80.00	28.42	0.5464	5.22
70.00	33.30	0.4776	5.20
Nickelbromid			
90.00	24.20	0.6162	5.27
80.00	28.45	0.5459	5.25
70.00	33.29	0.4777	5.28

Aus der Tabelle II ist ersichtlich, dass die Färbung des Komplexes bei konstantem pH-Wert unabhängig vom Anion ist, an das das Nickel gebunden in der Ausgangslösung vorlag. Hieraus ergeben sich aus der praktischen Anwendung grosse Erleichterungen, da man nicht an den Gebrauch bestimmter Säuren für die photometrische Bestimmung gebunden ist.

Einfluss verschiedener Puffersubstanzen

Wie man aus den bisherigen Darlegungen folgern kann, ist es notwendig, damit eine reproduzierbare Extinktion des Nickelkomplexes gewährleistet ist, einen bestimmten pH-Bereich einzuhalten. Man ist daher gezwungen in gut gepufferten Lösungen zu arbeiten. Es wurde überprüft, ob man in der Auswahl der Puffersubstanz eine grosse Auswahl hat oder nur wenige Substanzen geeignet sind. Hierzu wurde wie folgt vorgegangen.

Versuchsausführung. Zu einer Nickelsalzlösung mit 2.5 ml Salpetersäure 1 : 1 in 100 ml Lösung, welche 88.50 mg Nickel in Form von Nitrat enthielt, wurden wechselnde Mengen verschiedener Pufferlösungen und 20 ml Komplexonlösung 0.1 molar zugesetzt. Die erhaltenen Ergebnisse sind in der Tabelle III zusammengefasst wiedergegeben.

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TABELLE III

EINFLUSS VERSCHIEDENER PUFFERSUBSTANZEN

Messbedingung: Gerät Elko II mit Glühlampe, Filter S57E und 5.000 cm Küvetten

Pufferlösung	pH-Wert	Extinktion berechnet für 5.000 cm Küvetten	Durchlässigkeit in % abgelesen
10 ml Kaliumtetraborat 20%	7.91	0.6008	25.07
5 ml Kaliumtetraborat 20%	5.02	0.6061	24.77
7.5 ml Kaliumtetraborat 20%	5.62	0.6059	24.78
10 ml Natriumtartrat 20%	4.51	0.6061	24.78
20 ml Natriumtartrat 20%	4.59	0.6061	24.78
10 ml Natriumacetat 40%	4.21	0.6059	24.78
20 ml Natriumacetat 40%	4.88	0.6061	24.75
30 ml Natriumacetat 40%	5.02	0.6061	24.77
10 ml Ammoniumacetat 40%	4.98	0.6059	24.78
20 ml Ammoniumacetat 40%	5.21	0.6108	24.50
30 ml Ammoniumacetat 40%	5.40	0.6299	23.45

Vergleicht man die in der Tabelle III gefundenen Extinktionswerte mit der Art der benutzten Puffersubstanzen, so sieht man, dass Ammonsalze in grösserer Menge einen nicht vernachlässigbaren deutlichen Einfluss auf die Ausbildung der Extinktion haben. Es ist daher am besten, bei der praktischen Benutzung dieser Nickelbestimmungsmethode auf die Verwendung von Ammonsalzen am besten ganz zu verzichten. Falls zwingende Gründe im Analysengang vorliegen für die Benutzung von Ammoniumverbindungen, so muss darauf geachtet werden, dass immer die gleiche Menge Ammonsalze für die zu vergleichenden Analysen benutzt werden.

Die Erfüllung des Lambert-Beer'schen Gesetzes

Hierzu wurden Nickelsalzlösungen mit bekannten Gehalten in den Küvetten von 5.000 cm und 0.100 cm gemessen. Aus den erhaltenen Durchlässigkeitswerten wurde der dekadische Extinktionskoeffizient, bezogen auf mg Nickel in 100 ml, berechnet. Aus diesen Werten kann man dann ersehen, in welchen Grenzen das LAMBERT-BEER'sche Gesetz für die benutzte Reaktion gültig ist. Die Ergebnisse dieser Messungen sind in den Tabellen IV und V wiedergegeben.

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TABELLE IV

DIE ERFÜLLUNG DES LAMBERT-BEER'SCHEN GESETZES

Messbedingung: Gerät Elko II mit Glühlampe, Filter S57E und 5.000 cm Küvetten

mg Nickel in 100 ml	Extinktion für 5.000 cm Küvette	Extinktionskoeff. cm^{-1}/(mg Ni/100 cm^3)
90.00 mg	0.6162	0.00136
80.00 mg	0.5464	0.00136
70.00 mg	0.4774	0.00136

TABELLE V

DIE ERFÜLLUNG DES LAMBERT-BEER'SCHEN GESETZES

Messbedingung: Gerät Elko II mit Glühlampe, Filter S57E und 0.100 cm Küvetten

mg Nickel in 100 ml	Extinction für 0.1000 cm Küvette	Extinktionskoeff. cm^{-1}/mg Ni/100 ml
1800	0.2366	0.00136
3200	0.4377	0.00136
5000	0.6825	0.00136

Aus den vorstehenden Daten ersieht man, dass das LAMBERT-BEER'sche Gesetz in dem weiten Bereich von 40 bis 5000 mg Nickel in 100 ml Lösung streng erfüllt ist. Es ist daher möglich, Nickel nach dieser Methode in einem sehr weiten Konzentrationsbereich photometrisch bestimmen zu können.

Einfluss der überschüssigen Äthylendiamintetraessigsäure auf den Nickelkomplex

Für die praktische Durchführung der photometrischen Nickelbestimmung ist es wichtig zu wissen, welchen Einfluss ein Überschuss von Komplexon III auf die Ausbildung der Farbe des Nickelkomplexes ausübt. Zur Nachprüfung wurden

TABELLE VI

EINFLUSS DER ÜBERSCHÜSSIGEN ÄTHYLENDIAMINTETRAESSIGSÄURE AUF DEN NICKELKOMPLEX

Messbedingung: Gerät Elko II mit Glühlampe, Filter S57E und 5.000 cm Küvetten.

ml Komplexon-Lösung (0.1 molar)	pH-Wert	Extinktion für 5.000 cm Küvetten	Durchlässigkeit in % abgelesen
5	5.22	0.1773	66.48
10	5.19	0.3202	47.84
15	5.20	0.3372	46.00
20	5.21	0.3388	45.83
30	5.18	0.3381	45.90
40	5.20	0.3388	45.83

50.35 mg Nickel, die als Nitrat vorlagen, mit einer wechselnden Menge Dinatriumsalz der Äthylendiamintetraessigsäure (0.1 molar) versetzt und anschliessend mit 20 ml Natriumacetatlösung 20%ig als Pufferlösung zugefügt. Es wurde wieder mit Filter S57E in der 5.000 cm Küvette und der Glühlampe im Elko II gemessen. Die Ergebnisse sind in der Tabelle V wiedergegeben.

Aus den vorstehenden Tabellenwerten dieser Messungen ist ersichtlich, dass ein Überschuss der Komplexon-III-Lösung durchaus gestattet ist und keinen Einfluss auf die Ausbildung der Extinktion hat. Weiterhin ersieht man hieraus, dass man Nickelsalzlösungen auch direkt mit einer Lösung des Dinatriumsalzes der Äthylendiamintetraessigsäure titrieren kann, ohne dass man einen besonderen Metallindikator anwendet, lediglich durch Indikation des Umschlagpunktes auf lichtelektrischem Wege.

Aufstellung einer Eichkurve:

Wechselnde Mengen Nickel wurden in Form von Nickelnitrat in einen 100 ml Kolben gegeben, mit Natriumacetatlösung gepuffert und mit 20 ml einer Lösung des Dinatriumsalzes der Äthylendiamintetraessigsäure (0.1 molar) versetzt und zur Marke aufgefüllt. Die Messung wurde gegen Wasser mit Filter 57E und Glühlampe in 5.000 cm Küvetten im Elko II durchgeführt. Die erhaltenen Ergebnisse sind in der Tabelle VII wiedergegeben.

TABELLE VII

AUFSTELLUNG EINER EICHKURVE

Messbedingung: Gerät Elko II mit Glühlampe, Filter S57E und 5.000 cm Küvetten

mg Nickel in 100 ml	pH-Wert	Extinktion	Extinktionskoeff. mg Nickel in 100 ml
90.00	5.31	0.6162	0.00136
85.00	5.30	0.5851	0.00136
80.00	5.31	0.5464	0.00136
75.00	5.28	0.5133	0.00136
70.00	5.27	0.4774	0.00136
65.00	5.30	0.4424	0.00136
60.00	5.32	0.4063	0.00136
55.00	5.29	0.3711	0.00136
50.00	5.29	0.3359	0.00136
45.00	5.25	0.2989	0.00136
40.00	5.25	0.2642	0.00136

Mit vorstehenden Werten ist der Beweis gebracht, dass sich Nickel auch in grösseren Konzentrationen mit dieser Methode sehr exakt photometrisch bestimmen lässt.

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Vergleich mit bisherigen Methoden und technische Anwendung des Verfahrens

Mit den bekannten photometrischen Nickel-Bestimmungsverfahren, bei denen Nickel nach Fällung mit Dimethylglyoxim oxydiert[8] oder besser mit Chloroform ohne Oxydation ausgeschüttelt wird[1], kann man ohne zu grosse Verdünnungen herzustellen Nickelgehalte bis etwa 15% vorteilhaft bestimmen. Diese Nickelbestimmungsverfahren werden für höhere Legierungsgehalte an Nickel durch das beschriebene Verfahren ergänzt, das sich durch besondere Einfachheit in der Ausführung auszeichnet. So konnten wir im Monel-metall das Nickel sehr exakt und schnell bestimmen.

ZUSAMMENFASSUNG

Es wird gezeigt, dass der Nickelkomplex der Äthylendiamintetraessigsäure im pH-Bereich 4.55 bis 6.82 für die photometrische Bestimmung hoher Nickelgehalte herangezogen werden kann. Die Durchlässigkeitskurve des Komplexes zeigt, dass mit dem Gerät Elko-II und mit Hilfe des Filters S57E und der Glühlampe gut reproduzierbare Messwerte erhalten werden. Grössere Mengen Ammonsalze haben einen deutlichen Einfluss, sodass man solche Salze vermeiden soll. Der Komplex ist von dem Anion der Nickelverbindungen unabhängig. Das LAMBERT-BEER'sche Gesetz ist im Bereich von 40 bis 5000 mg Nickel pro 100 ml/Lösung erfüllt. Das Verfahren ist für die Untersuchung hoch-nickelhaltiger Metallegierungen geeignet.

SUMMARY

It is possible to determine very high concentrations of nickel photometrically by means of ethylenediaminetetra-acetic acid, by working at a pH between 4.55 and 6.82. The absorption curves obtained for this complex are very reproducible; for these measurements an Elko II apparatus with filter S57E is used. High concentrations of ammoniacal salts hinder the measurement. The formation of the complex is not influenced by the anion of the compound of nickel used. The LAMBERT-BEER law is followed for strengths of nickel of 40 — 5000 mg/100 ml. This procedure is convenient for alloys rich in nickel.

RÉSUMÉ

Il est possible de doser photométriquement de fortes teneurs en nickel, au moyen de l'acide éthylènediaminotétraacétique, en travaillant à un pH compris entre 4.55 et 6.82. Les courbes d'absorption obtenues pour ce complexe sont très reproductibles; on utilise pour ces mesures un appareil Elko-II avec filtre S57E. De fortes teneurs en sels ammoniacaux gênent. La formation du complexe n'est pas influencée par l'anion du composé du nickel utilisé. La loi de LAMBERT-BEER est suivie pour des teneurs en nickel de 40 à 5000 mg/100 ml. Ce procédé convient pour les alliages riches en nickel.

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APPLICATION OF ABSORPTION SPECTRUM OF SODIUM VANADATE TO DETERMINATION OF VANADIUM *

by

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The purpose of the present work was to study the ultraviolet absorption characteristics of sodium vanadate in one molar sodium hydroxide solution. Water solutions of vanadates are known to be sensitive to change from one species or form to another with change in pH of the solution[1], *viz.*,

$$VO_4^{-3} \rightleftharpoons \overset{\overset{OH^-}{\longleftarrow}}{\underset{\underset{H^+}{\longrightarrow}}{V_2O_7^{-4}}} \rightleftharpoons VO_3^-$$

In a one molar sodium hydroxide solution, only the orthovanadate, VO_4^{-3}, exists. It was found that the properties of the vanadate in this concentration of alkali could be applied to the quantitative estimation of small amounts of vanadium providing interfering ions were removed.

Chromate and manganate ions showed appreciable absorption in the same region as the vanadate (270 mμ wavelength), whereas the tungstate, phosphate, aluminate and zincate did not appear to interfere. The spectral transmittancy curves of these ions in one molar sodium hydroxide solution are shown in Fig. 1. In applying the method to the analysis of rocks, minerals and ores containing appreciable amounts of chromium and manganese, it was found necessary to extract the vanadium with 8-hydroxyquinoline and chloroform[2]. It was found that, under the conditions of this work, a one molar sodium hydroxide solution did not cause changes in the transmittancy of the quartz cells through etching. The sodium hydroxide solutions were allowed to remain in the cells only long enough to obtain the readings.

Preparation of vanadate solutions

The vanadate stock solutions were prepared by dissolving 2.000 g of Eimer and Amend Brand C.P. grade ammonium metavanadate in 1 liter of distilled

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* Abstracted from a portion of a dissertation presented by IRWIN M. GOTTLIEB to the faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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water in a calibrated volumetric flask with a final concentration of 0.871 mg vanadium per ml. Dilutions of this stock solution were made with freshly prepared 1 molar sodium hydroxide solution, and used for the spectrophotometric measurements. The solutions were allowed to stand at least $^1/_2$ hour to reach equilibrium before a determination of the absorption spectrum was made.

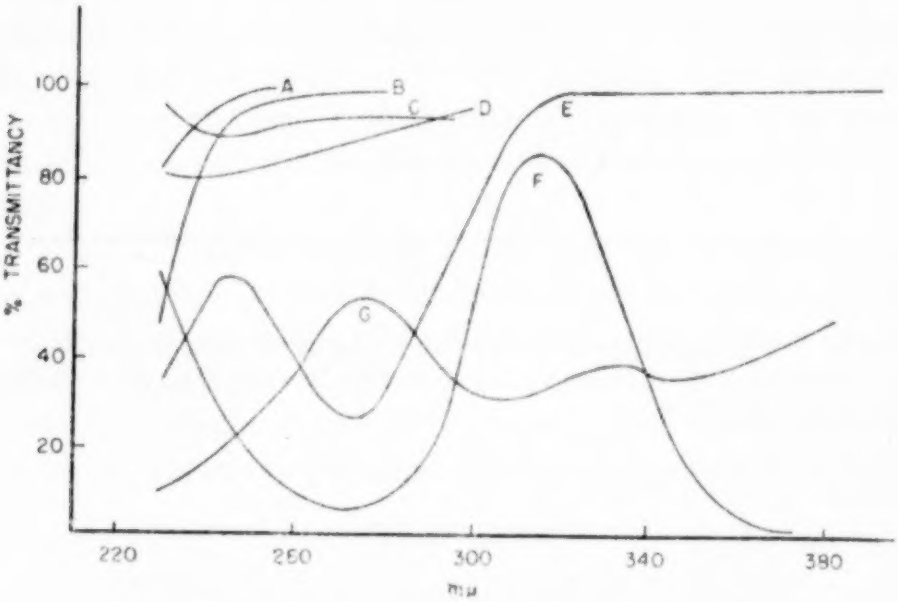

Fig. 1. Typical spectral transmittancy curves in 1*M* sodium hydroxide. *A* — zincate, *B* — tungstate, *C* — phosphate, *D* — aluminate, *E* — vanadate, *F* — chromate, G — manganate.

Instrumentation

Measurements of per cent. transmittancy and optical densities were made by means of a Model DU Beckman spectrophotometer. Previously calibrated 1.000 cm silica cells were used. The cells were cleaned with distilled water and spectroscopically pure methanol each time the solution was changed. The reference cell contained one molar sodium hydroxide solution during the measurements. All optical densities and per cent. transmittancies are an average of at least three individual readings.

The absoption spectrum in the ultraviolet region (230-330 mμ range) was obtained for the orthovanadate ion in one molar sodium hydroxide solution in the concentration range of $0.435 \cdot 10^{-3}$ mg to $43.5 \cdot 10^{-3}$ mg of vanadium per ml. The curves are given in Fig. 2. Examination of the curves indicates that the absorbancy maximum for this ion in one molar sodium hydroxide occurs in the vicinity of 270 mμ. A plot of vanadium concentration versus optical density at this wave length is shown in Fig. 3. The straight line indicates that BEER's Law is obeyed and that the absorption maximum at 270 mμ may be used for the quantitative estimation of vanadium.

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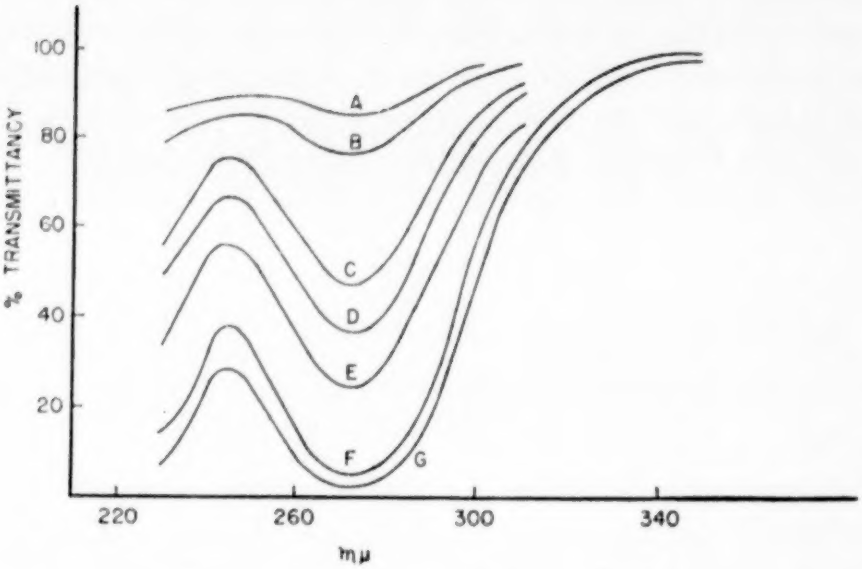

Fig. 2. Spectral transmittancy curves of sodium orthovanadate in 1*M* sodium hydroxide. *A* — 0.435, *B* — 0.871, *C* — 2.18, *D* — 3.05, *E* — 4.35, *F* — 8.71, *G* — 10.9. micrograms V/ml.

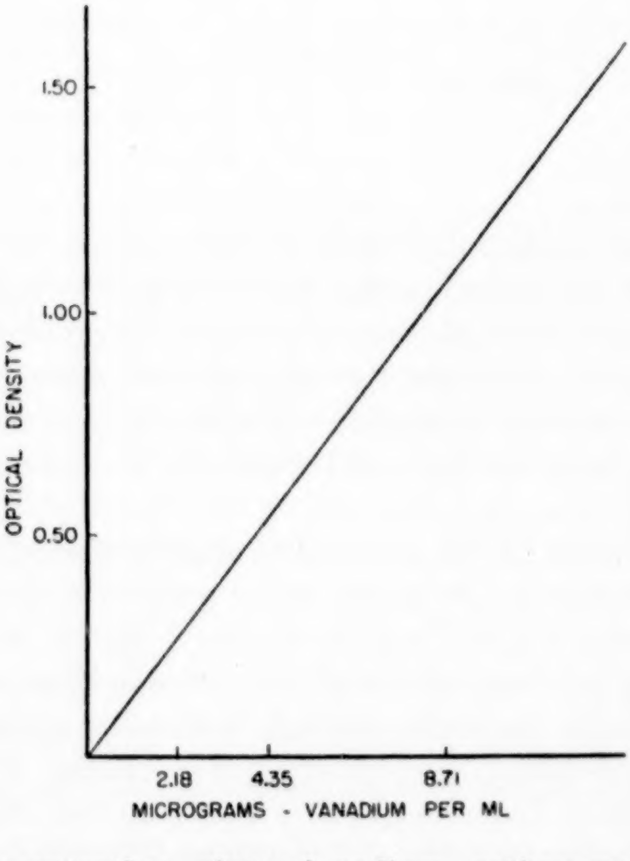

Fig. 3. Density concentration plot of sodium orthovanadate in 1*M* sodium hydroxide solution at wavelength 270 mμ.

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Procedure for the determination of vanadium in ores, rocks and minerals

One gram sample of the powdered material is fused with 5 or 6 grams of anhydrous sodium ca rbonate in a platinum crucible. After the decomposition is complete, allow the crucible to come to room temperature. Place the crucible in a Pyrex beaker of convenient size and add 5-10 ml of distilled water. Heat to boiling and place on a steam bath. Disintegrate the cake by crushing and grinding with a flattened glass rod. When the residue has become entirely decomposed, add 3-5 ml of reagent grade methyl alcohol to reduce the manganate. Heat just to boiling and filter the solution through a fine grained paper (*e.g.*, Whatman's No. 42), wash with hot water and dilute the filtrate and washings to 100 ml in a calibrated volumetric flask.

Pipette 10 or 20 ml of this solution (depending on the amount of vanadium in the original sample) into a small Erlenmeyer flask, and add 1-2 drops of methyl orange indicator solution. Then add $4N$ sulfuric acid from a pipette or buret until the solution assumes the intermediate color of the indicator. Swirl the solution to expel the carbon dioxide and transfer to a small separating funnel. Add 2-3 drops of an 8-hydroxyquinoline solution (2.5 per cent. in 1:8 acetic acid),

TABLE I

DETERMINATION OF VANADIUM IN IRON ORES

Sample		Proposed method Vanadium %	Analyst value* Vanadium %
1.		0.034	
		0.035	
		0.040	
	Ave.	0.036	0.032
2.**		0.065	
		0.040	
	Ave.	0.052	0.045
3.		0.69	
		0.60	
		0.58	
	Ave.	0.62	0.64
4.		0.23	
		0.25	
		0.31	
		0.32	
	Ave.	0.28	0.28

* The Analyst value reported by the Bethlehem Steel Company gives the average obtained by several different chemists. Ten gram samples were used. The iron was removed by extraction and the vanadium determined volumetrically or colorimetrically.

** Probably the large difference is due to sampling.

TABLE II

DETERMINATION OF VANADIUM IN FLINT CLAY AND PLASTER CLAY

Sample		Proposed method	Bureau of standards*
		V_2O_5 %	V_2O_5 %
B.S. ≠97		0.039	
		0.043	
	Ave.	0.041	0.040
B.S. ≠98		0.034	
		0.026	
		0.027	
		0.031	
	Ave.	0.029	0.025

* These results were reported by the Bureau of Standards.

and extract with 2-3 ml of reagent grade chloroform. Shake for one minute to extract the blackish vanadium-oxine complex. Allow the chloroform layer to settle, then draw it off into a platinum crucible. Rinse out the stem of the funnel with a milliliter of chloroform. Repeat the extraction until the last portion of chloroform shows only a faint yellow color due to the reagent itself.

Add about 0.1 gram of anhydrous sodium carbonate to the crucible containing the combined extracts, and evaporate at low temperature on a steam bath. Heat the crucible to destroy the organic matter and fuse the sodium carbonate for 1-2 minutes in order to convert the vanadium to sodium vanadate. Dissolve the melt in 10-15 ml of water and add 4 grams of reagent grade sodium hydroxide. The solution at this point should be clear. If it is not clear, filter through a small porous porcelain or sintered glass crucible. Transfer the filtrate and washings to a 100 ml calibrated volumetric flask. Cool to room temperature and dilute to the mark with distilled water. Mix thoroughly and measure the optical density at wavelength of 270 mμ against a blank solution containing one molar sodium hydroxide solution. The concentration of the unknown can be determined from the optical density-concentration curve obtained using pure vandate salt in one molar sodium hydroxide solution, as shown in Figure 3. The accuracy that can be expected from the application of the present method to the analysis of rocks and minerals containing small amounts of vanadium is shown by the data in Tables I and II.

SUMMARY

A method is proposed for the determination of small amounts of vanadium as found in certain ores, rocks and minerals. After fusion of the sample, the 8-hydroxyquinoline complex is extracted with chloroform and converted to sodium orthovanadate. The absorbancy of this compound is measured at a wavelength of 270 mμ. The present method does not depend on the formation of a colored complex and, hence, is independent of such conditions as time and temperature.

RÉSUMÉ

Une méthode est proposée pour le dosage de faibles teneurs de vanadium dans certains minerais. Après fusion de l'échantillon, le complexe obtenu avec la 8-hydroxyquinoléine est extrait par le chloroforme et transformé en orthovanadate de sodium. L'absorption de ce composé est mesurée à la longueur d'onde de 270 mμ. Cette méthode, ne dépendant pas de la formation d'un complexe coloré, ne subit pas par conséquent l'influence du temps et de la température.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen für die Bestimmung von kleinen Quantitäten von Vanadium in gewissen Mineralien. Nach dem Schmelzen der Probe, wird der mit 8-Hydroxychinolin erhaltene Komplex mit Chloroform ausgezogen und in Form von Natrium-Orthovanadat gebracht. Die Absorption dieser Verbindung wird bei einer Wellenlänge von 270 mμ gemessen. Da diese Methode nicht von der Bildung eines gefärbten Komplexes abhängt, wird sie weder durch die Arbeitszeit noch durch die Temperatur beeinflusst.

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KONZENTRATIONSPOLARISATION IN EINER QUECKSILBERLÖSUNG BEI ELEKTROLYSE ZWISCHEN ZWEI QUECKSILBERELEKTRODEN

von

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EINLEITUNG

Als erste Ausführung einer „dead-stop"-Titration, bei der zwischen zwei gleichen Elektroden eine nahezu konstante (geringe) Spannung angelegt wird und der Strom als Funktion der hinzugefügten Reagensmenge[1] gemessen wird, kann das Werk SALOMONS[2,3] betrachtet werden. Die Art der Ausführung war etwas anders; weder die Flüssigkeit noch die Elektroden wurden rotiert. Die Folge davon war, dass es lange dauerte, bis der stationäre Zustand eintrat, während dies heutzutage praktisch sofort erfolgt.

SALOMON untersuchte Systeme mit zwei Elektroden des Metalls M in einer Lösung M^{+z_i}. Diese Kombination ist in der neueren Literatur nahezu unbekannt. M war Ag, Hg und Cu.

Im Nachstehenden wird die mathematische Behandlung SALOMONS, wie sie im zweiten Artikel verbessert wiedergegeben ist, etwas weiter fortgesetzt, wobei vorausgesetzt wird, dass durch den grossen Überschuss des Grundelektrolyts der Migrationsstrom des Ions M^{+z_i} vernachlässigbar ist. Es wird sich dann erweisen, dass die Einstellzeit beim alten Verfahren sehr bedeutend ist. Ausserdem wird von dem Verhältnis zwischen Stromstärke, Spannung und Konzentration eine andere Ableitung gegeben werden, die den neueren Einsichten[4,5] über diese Titrationsmethode entspricht. Das Ergebnis dieser letzten Ableitung wird mit den Resultaten einiger Versuche verglichen werden.

EINSTELLZEIT FÜR EINEN STATIONÄREN ZUSTAND BEIM ALTEN VERFAHREN

Erklärung der benutzten Symbole;

C = Konzentration (Gramm-Ionen pro Milliliter)

C_{An} = Konzentration an der Anode

C_K = Konzentration an der Kathode

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C_o = ursprüngliche Konzentration

$\gamma = \frac{C}{C_o}$ = relative Konzentration

$\delta = \frac{C_{An} - C_o}{C_o} = \frac{C_o - C_K}{C_o}$

D = Diffusionscoefficient ($\text{cm}^2.\text{sec}^{-1}$)

l = Elektrodenabstand (cm)

t = Zeit (sec)

Man stelle sich eine horizontale, von zwei Parallelelektroden abgeschlossene Röhre vor. Der Abstand von einem Punkt im Zwischenraum bis zur linken Elektrode, die als Kathode fungieren wird, kann durch ξl angegeben werden.

Die Diffusionsgleichung für das Ion M^{+z_i} lautet dann:[6]

$$\frac{\partial C}{\partial t} = \frac{D}{l^2} \cdot \frac{\partial^2 C}{\partial \xi^2}$$

oder

$$\frac{\partial \gamma}{\partial t} = \frac{D}{l^2} \cdot \frac{\partial^2 \gamma}{\partial \xi^2}$$

Mit den Randbedingungen:

$$\left.\begin{array}{l} \xi = 0 \; : \; \gamma = 1 - \delta \\ \text{und} \\ \xi = 1 \; : \; \gamma = 1 + \delta \end{array}\right\} \; t > 0 \, ; \; t = 0 : \gamma = 1$$

findet man als Endergebnis der Integration[7]:

$$\gamma = 1 + \delta\,(2\xi - 1) + \frac{2\delta}{\pi} \sum_{k=1}^{k=\infty} \frac{1}{k} \cdot e^{-\frac{4\pi^2 k^2 . D . t}{l^2}} \sin 2\pi\, k . \xi$$

Diese Funktion ist in Abb. 1 für einige Werte von t wiedergegeben.

Die Stromstärke ist proportional zu $\frac{\partial \gamma}{\partial \xi}$ für $\xi = 0$.

$$\left[\frac{\partial \gamma}{\partial \xi}\right]_{\xi = 0} = 2\delta + 4\delta \sum_{1}^{\infty} e^{-\frac{4\pi^2 k^2 . D . t}{l^2}}$$

Annährend gilt, dass die Zeit t, die verfliesst, bevor die Stromstärke bis zu p% über ihrem Endwert gefallen ist, durch folgenden Ausdruck dargestellt werden kann (vorausgesetzt, dass p nicht zu klein ist):

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$$t = \frac{l^2}{(1 + \frac{p}{100})^2 \, 4\pi \, D}$$

Man ermittelt die Zeiten t_1 und t_2, bei denen die Stromstärken 100% bezw. 5% über ihrem Endwert liegen:

$t_1 = 0.0205 \, l^2/D$; $t_2 = 0.0935 \, l^2/D$

Da D ungefähr 10^{-5} cm² sec⁻¹ beträgt, ergibt sich hieraus, dass bei einem Elektrodenabstand von 1 cm $t_1 = 2 \cdot 10^3$ sec und $t_2 = 9 \cdot 10^3$ sec. Diese Zeiten sind so bedeutend, dass es fraglich ist, ob SALOMON lange genug wartete. Er berichtete nur, dass er wartete, bis in einem Zeitraum von 5 Minuten keine bemerkbare Änderung der Stromstärke festgestellt werden konnte. Dass dieses Kriterium leicht zu einem irrtümlichen Wert führen kann, zeigt uns die Betrachtung eines gleichartigen Versuches von LAITINEN UND KOLTHOFF[8].

Eine andere experimentelle Fehlerquelle ist das Auftreten von Konvektion infolge von Unterschieden in der Dichte. Auf jeden Fall liegen die früheren Beobachtungen auf einer Kurve, die bei kleinen Spannungen eine andere Form aufweist, als dies theoretisch zu erwarten wäre.

THEORETISCHE ABHÄNGIGKEIT ZWISCHEN STROM, SPANNUNG UND KONZENTRATION

Siehe die Reaktion an der Elektrode:

$M^{+z_i} + z_i \, e \rightleftarrows M$

Das Potential des Metalls in bezug auf die Flüssigkeit kann wiedergegeben werden durch:

$$E = E_0 + \frac{R.T}{z_i \cdot F_y} \ln {}^{\circ}C \quad \ldots\ldots\ldots\ldots \quad (1)$$

wenn $°C$ die Konzentration von M^{+z_i} an der Elektrodenoberfläche darstellt.

Durch das Auftreten von Diffusion besteht die Beziehung:

$$^{*}C - {}^{\circ}C = a.i. \quad \ldots\ldots\ldots\ldots \quad (2)$$

wenn $*C$ die Konzentration in relativ grossem Abstand von der Elektrode darstellt; die Stromstärke i wird positiv genommen, wenn es sich um die Kathode handelt.

Die Kombination von (1) und (2) gibt uns

$$E = E_0 + \frac{R.T}{z_i \cdot F_y} \ln ({}^{*}C - a.i)^{9} \quad \ldots\ldots\ldots\ldots \quad (3)$$

Aus der Betrachtung von Abb. 2 geht deutlich hervor, dass bereits bei einem kleinen Spannungsunterschied zwischen den Elektroden ein Stromdurchgang stattfinden wird. Wenn dieser Spannungsunterschied △ ist, ergibt sich aus Gleichung (3), wenn man bedenkt, dass der Wert des Anodenstroms dem Kathodenstrom absolüt gleich ist, aber negativ genommen wird:

$$\Delta = E_{An} - E_K = \frac{R.T}{z_i \cdot F_y} \ln \frac{*C + a.i}{*C - a.i} \qquad (4)$$

Diese Gleichung ist nach i lösbar:

$$i = \frac{*C}{a} \cdot \frac{\Delta' - 1}{\Delta' + 1} \qquad (5)$$

wenn zur Abkürzung geschrieben wird:

$$\Delta' = e^{\Delta \Big/ \frac{R.T}{z_i \cdot F_y}} \qquad (6)$$

Auch SALOMON fand ein ähnliches Verhältnis zwischen i und Δ'. Im Falle einer rotierten Flüssigkeit wird die Konzentration einen Verlauf haben, wie er in Abb. 1 für einen sehr kurzen Zeitraum angegeben wird.

WAHL DES UNTERSUCHTEN SYSTEMS

Die Untersuchungen von RIUS[10] zeigen deutlich, dass es sich bei Silber nicht ausschliesslich um Polarisationskonzentration handelt, wenn FIANDA UND NAGEL[11] auch anderer Meinung sind. Kupfer ist in dieser Hinsicht noch weniger geeignet[12]. Die ersten Beobachtungen wurden mit einer Mercuronitratlösung in einem Grundelektrolyt von 5M Natriumnitrat und 0.8N Salpetersäure gemacht. Besonders jedoch die Beobachtungen bei hohen Spannungen waren nicht gut reproduzierbar

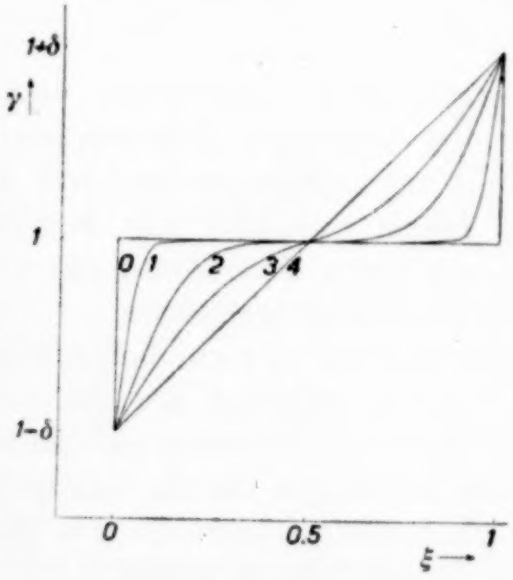

Abb. 1. Relative Konzentration zwischen Kathode und Anode auf verschiedene Zeitpunkten nach dem Anfang der Electrolyse.

0 $t = 0$

1 $t = \frac{l^2}{1000\ D}$

2 $t = \frac{l^2}{100\ D}$

3 $t = \frac{l^2}{35\ D}$

4 $t = \infty$

Zuverlässige Beobachtungen waren im Vorhandensein von 5M Natriumnitrat und 0.6M Kaliumjodid möglich.

Die Elektrodenreaktion, die in der Polarographie bereits Anwendung[13] gefunden hat, ist hier:

$$HgI_4^{-2} + 2e \rightleftarrows Hg + 4I^-$$

$$E = E_o + \frac{R.T}{2F_y} \ln {}^{\circ}C_{Hg^{+2}} \qquad \ldots\ldots \qquad (7)$$

Ferner besteht das Gleichgewicht

$$Hg^{+2} + 4I^- \rightleftarrows HgI_4^{-2}$$

wofür gilt:

$$K = \frac{[Hg^{+2}] \cdot [I^-]^4}{[Hg\,I_4^{-2}]} \qquad \ldots\ldots \qquad (8)$$

Aus (7) und (8) ergibt sich dann:

$$E = E_o + \frac{R.T}{2F_y} \ln K \frac{{}^{\circ}[HgI_4^{-2}]}{{}^{\circ}[I^-]^4} \qquad \ldots\ldots \qquad (9)$$

Durch den grossen Überschuss des Jodids werden die Konzentrationen hiervon an der Elektrode vernachlässigbar kleine relative Änderungen erfahren (die absoluten Änderungen sind ungefähr das Vierfache der Konzentrationsänderung des Jodomercurats). Die Gleichung (9) kann daher vereinfacht werden zu

$$E = E_o' + \frac{R.T}{2\,F_y} \ln {}^{\circ}[HgI_4^{-2}] \qquad \ldots\ldots \qquad (10)$$

welche Gleichung mit (1) übereinstimmt. Die weitere Ableitung bleibt also dieselbe.

VERSUCHE

Die Elektrolyse wurde in einem *Perspex*behälter (Acrylharz) ausgeführt (Durchmesser 5 cm, Höhe 12 cm). Die beiden Höhlungen (Durchmesser 2 cm) im Boden wurden mittels eines Hahntrichters mit kapillärem Stiel mit Quecksilber gefüllt, nachdem der Behälter mit Inhalt gründlich mit Kohlensäure durchgespült war. Das Quecksilber war durch einen Platindraht mit einer an der Aussenseite angebrachten Steckbuchse stromleitend verbunden.

Auf dem Boden zwischen den Elektroden war ein ±1 cm hohes Plättchen angebracht, wodurch die Quecksilberoberflächen während des Rührens viel weniger Deformierung erfuhren. Der Deckel wurde mit Klemmen auf den Flansch des Behälters befestigt. Dieser Deckel hatte Öffnungen für die Gaszufuhr, die Bürette und den Flügelrührer, der durch einen Drehstrommotor mit einer Geschwindigkeit von 1350 Umdrehungen pro Minute bewegt wurde.

Die elektrische Schaltung ist schon früher gegeben[14]. Als Galvanometer diente der Radiometer G.V.M.11, als Spannungsmesser das Philips-Gerät GM 6010.

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In der ersten Reihe Beobachtungen wurde nachgeprüft, ob es sich hierbei um das lineäre Verhältnis zwischen i und $\frac{\Delta' - 1}{\Delta' + 1}$ handelt.

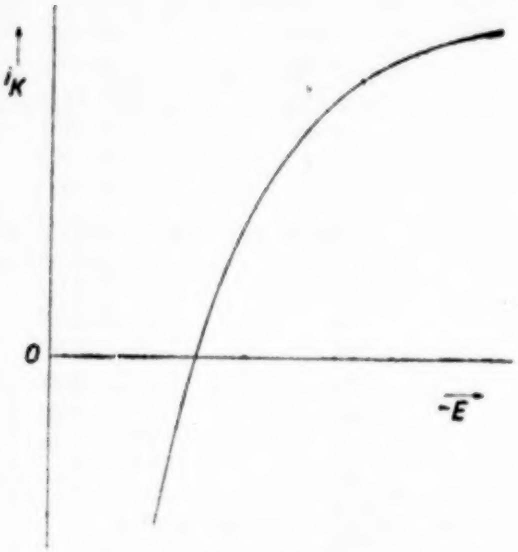

Abb. 2. Polarogramm einer Quecksilbersalzlösung an einer Queksilber-Elektrode.

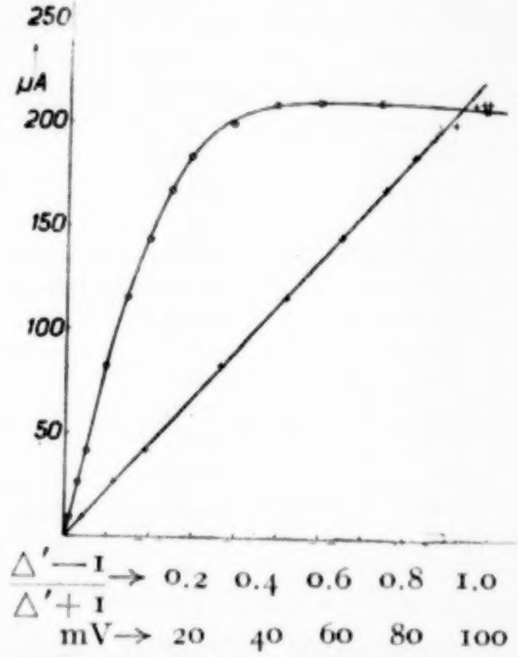

Abb. 3. Strom als Funktion der korrigierten Spannung (o) und als Funktion von $\frac{\Delta' - 1}{\Delta' + 1}$ (x)

Die Daten sind in Tabelle I gegeben, während die Ergebnisse in Abb. 3 aufgezeichnet sind. Die zwischen den Elektroden gemessene Spannung wurde für den ohmischen Spannungsabfall, der in der Lösung stattfindet, korrigiert.

Die zweite Versuchsreihe bezog sich auf das Verhältnis zwischen Strom und Konzentration. Die Stromstärke wurde in diesem Falle sowohl für die Volumenzunahme wie auch für den in der Lösung stattfindenden Spannungsabfall korrigiert.

Die Beobachtungen und Berechnungen sind in Tabelle 2 aufgenommen und in Abb. 4 dargestellt.

Während die erste Versuchsreihe über ein grosses Spannungsgebiet den Erwartungen entspricht, kommt in der zweiten Reihe eine Abweichung vom lineären Verhältnis zwischen Stromstärke und Konzentration vor, das der Ableitung gemäss hätte existieren sollen. Dies schliesst jedoch eine Anwendung in der Analyse nicht aus, was aus einer folgenden Veröffentlichung hervorgehen wird.

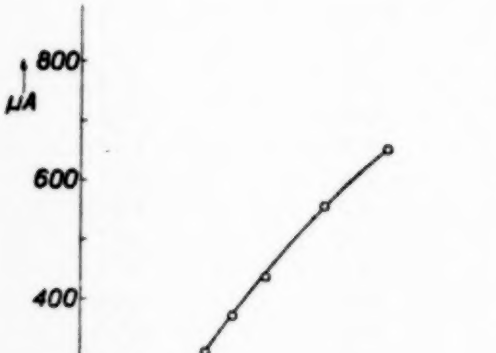

Abb. 4. Strom als Funktion der Konzentration bei Konstanter Spannung.

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TABELLE I

$\triangle$ unkorrigiert mV	i μA	$i.R$ mV	$\triangle$ korrigiert mV	$\frac{\triangle' - 1}{\triangle' + 1}$
1.00	8.7	0.04	0.96	0.038
3.00	26.2	0.11	2.89	0.115
5.00	41.3	0.17	4.83	0.190
10.00	82.2	0.34	9.66	0.367
15.0	115	0.47	14.5	0.523
20.0	144	0.59	19.4	0.649
25.0	167	0.69	24.3	0.749
30.0	183	0.75	29.3	0.823
40.0	199	0.82	39.2	0.917
50	208	0.86	49	0.962
60	209	0.86	59	0.982
75	209	0.86	74	0.994
100	206	0.86	99	0.999
150	207	0.86	149	1.000
200	238	1.00	199	1.000
300	232	1.00	299	1.000
500	220	0.93	499	1.000

Zusammensetzung der Lösung:

120 ml $5M$ $NaNO_3$, 1 ml Eisessig, 10 g KJ, 6 ml $4^0/_{00}$ Gelatine, 1 Tropfen Octylalcohol, $\frac{1}{2}$ ml Hg(II) $1/20M$. Widerstand zwischen die Elektroden: 4.1 Ω. Temperatur: 18° C.

TABELLE II

ml $^1/_{20}$ M Jodomercurat	i μA gemessen	$i.R$ mV	$\triangle$ mV korrigiert	i μA korrigiert *
0.00	3.89	0.02	10.0	3.9
0.20	33.4	0.14	9.9	33.9
0.43	71.3	0.29	9.7	73.7
0.605	98.3	0.40	9.6	103
0.805	126	0.52	9.5	134
1.035	155	0.64	9.4	167
1.505	213	0.87	9.1	236
2.05	269	1.10	8.9	307
2.51	317	1.30	8.7	371
3.03	363	1.49	8.5	437
4.005	441	1.81	8.2	556
5.025	498	2.04	8.0	651

Zusammensetzung von 125 ml der Lösung:

12 g KJ, 1 ml Eisessig, 6 ml Gelatine $4^0/_{00}$, 2 g Natriumsulfit, Rest $NaNO_3$ $5M$.
Temperatur 22° C, Widerstand 4.1 Ω.
Spannung zwischen die Elektroden: 10.0 ± 0.1 mV.

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* Korrektion auf 10.0 mV und 125 ml.

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ZUSAMMENFASSUNG

Es wird eine theoretische und praktische Darstellung gegeben von einer ,,Dead-stop''-Titration mit Quecksilberelektroden in einer Quecksilbersalzlösung.

SUMMARY

The theoretical and practical behavior of mercury electrodes in a mercury salt solution using a dead-stop circuit are described.

RÉSUMÉ

L'auteur fait un exposé théorique et pratique d'une titration ,,dead-stop'' avec électrodes de mercure et une solution d'un sel de mercure.

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RAPID METHOD FOR THE SEPARATION AND DETERMINATION OF BISMUTH, ANTIMONY, AND TIN BY CONTROLLED CATHODE ELECTROANALYSIS*

by

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The aim of this investigation was to devise a procedure, utilizing the techniques of controlled cathode potential electrolysis, whereby bismuth, antimony, and tin could be rapidly deposited successively onto a platinum cathode. The influence on the electrodeposition caused by various inorganic anions, organic masking agents, hydrogen-ion concentration, temperature of the solution, and deposition potentials was studied systematically. The data thus obtained enabled a satisfactory electroanalytical procedure for the determination of bismuth, antimony and tin to be established.

Electrolytic separations by the constant current method depend on the use of 'potential buffers'. If, however, the cathode potential is maintained at a value sufficiently high to deposit quantitatively one metal, while remaining too low to deposit a second, separations can be achieved. This technique, known as electroanalysis with controlled or limited cathode potential was devised by SAND[11].

Bismuth has been electrodeposited from perchloric acid[9] and nitrate-fluoride-tartrate[2] systems. With controlled cathode potential techniques, bismuth has been plated from various electrolyte systems: sulfate and nitrate[5], tartrate[8], alkaline cyanide-tartrate[6], and chloride-oxalate[4]. Antimony has been determined by deposition from sulfuric-hydrochloric acid mixture[10] and from thioantimonite solution (with high results)[13]. It has been determined by controlled cathode methods from hydrochloric acid[12], sulfuric acid[11], and tartrate-sulfate solution[7]. Tin has been determined by the constant current method from hydrochloric acid solution, and oxalic acid-ammonium oxalate mixture[13]. Using the controlled cathode method, tin has been deposited from hydrochloric acid[1], and hydrochloric acid-tartaric acid solutions[8]. However, none of these procedures were found adaptable to the rapid, routine determination of bismuth, antimony, and tin successively.

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* From the M.S. Thesis of SAM A. REYNOLDS.

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APPARATUS AND REAGENTS

Electrodeposition equipment

Electrolyses were made with a Sargent-Slomin Electrolytic Analyzer. This device consists essentially of a Variac for control of the applied voltage, a 10/110 volt stepdown transformer, a selenium rectifier, a choke-condenser combination to remove most of the current ripple, and a voltmeter and ammeter in the output circuit. A second external, 0 to 150 milliamperes, ammeter was connected with the instrument's 0 to 10 ammeter by means of a double-throw switch in order to permit the reading of currents from one milliampere to several amperes.

The instrument employs a rotor for the anode and a stationary cathode. Electrodes were the conventional, large area, corrugated gauze type. This instrument has a rheostat-controlled heating surface for the electrolysis beaker.

The cathode potential was measured with a Beckman pH meter, model H-2. A small, micro calomel electrode was placed adjacent to the outside surface of the cathode near its middle.

pH Measurements

All pH measurements were made with a second Beckman glass electrode pH meter, model H-2.

For tracer studies a scintillation gamma counter was employed. Samples were placed in cup-type planchets supported over the crystal by means of a slide with a well into which the planchets were fitted.

Bismuth

Bismuth metal, assaying 99.8 per cent., was weighed directly. The concentration of antimony was less than 0.01 per cent.

Antimony

C. P. metal was assayed by dissolution in sulfuric acid and titration with permanganate. Triplicate results yielded an average of 99.64 per cent. antimony, with a mean deviation of 0.08 per cent. Spectroscopic analysis showed the presence of a small amount of lead, which was found to be 0.3 per cent. by electrodeposition and by polarography.

Tin

C. P. tin metal, assaying 100 per cent., was weighed directly.

Radioactive tracers

The antimony radioisotope employed in the tracer studies was antimony-124; the tin tracer was tin-113 with its indium-113 daughter. Both tracers were purified before use.

GENERAL EXPERIMENTAL TECHNIQUE

Weighed samples of the metals under study were dissolved in an appropriate acid, using the same beaker which was to serve for electrolysis. The solution was diluted somewhat, then the other materials, such as masking agents and depolarizers, were added, and the final dilution to the desired volume was made. This volume generally was 120 to 140 milliliters. The solution was heated when necessary during electrolysis by means of the heating unit of the Sargent-Slomin apparatus.

The potential of the cathode was controlled against a saturated calomel reference electrode, whose tip was placed close to the outside of the cathode near its middle. If the proper cathode potential was not known beforehand for a given system, an approximate value was determined by increasing the cathode potential until the ammeter showed a small current flowing and plating was noticeable on the cathode. The potential of the metal ion/metal-coated cathode was then determined by opening the plating-circuit current and noting the cathode-reference cell potential on the auxiliary Beckman pH meter. During deposition, the cathode potential was maintained 0.1 to 0.2 volt more negative than the initial value of the metal-coated cathode reduction potential.

After each deposition the cathode was washed with a stream of distilled water as it was withdrawn from the solution, then immersed twice in separate beakers of distilled water (since the solutions were usually high in total salt concentration), and immersed once in pure acetone. The cathode was dried in a gentle stream of dry-filtered air at room temperature to preclude any danger from air oxidation at elevated temperatures.

When a tracer was used, it was added at the beginning of the dissolution procedure to ensure that interchange took place.

Anodic oxidation of antimony and tin was prevented by the use of hydrazine or hydroxylamine as "anodic depolarizers." The former reagent was also used to reduce any pentavalent antimony to the trivalent condition before deposition. This was done by heating with hydrazine in concentrated sulfuric acid[3].

ELECTROLYTE SYSTEMS INVESTIGATED

Solutions were prepared by dissolving the metals in concentrated sulfuric acid with gentle heating, cooling the sample to within the range 50° to 70° C, and adding one gram of hydroxylamine or hydrazine sulfate to serve as the anodic depolarizer. The advantages of the sulfuric acid attack include the ease of dissolution of small quantities of sample, plus the fact that only a slight oxidation of antimony occurs. Next, a suitable quantity of complexing agent was added, and the pH and the temperature of the solution were adjusted to the desired values. Electrolysis was begun and continued until the current decreased to a small, constant value, usually less than 10 milliamperes. The time required for complete deposition varied from 25 minutes for bismuth to 50 minutes for tin.

Determinations of bismuth, antimony, and tin were most successful when these metals were deposited from a citrate-sulfate electrolyte, $0.2M$ in citrate and adjusted to pH 3. Bismuth was removed at a potential of -0.3 volt (vs. S.C.E.),antimony was deposited at the same potential after adding sufficient hydrochloric acid to adjust its concentration between 0.9 to 1.3 molar. Finally, using a clean electrode, tin was deposited at a potential of -0.65 volt (vs. S.C.E.).

The electrolysis time was considerably shortened by carrying out the depositions at 50-70° C. Typical results are summarized in Table I. Results were slightly high for bismuth; however a bias of $+1.3$ mg appears to be independent on the amount of bismuth plated. A similar negative bias of -1.2 mg was found for tin.

TABLE I

ANALYSIS OF MIXTURES OF BISMUTH, ANTIMONY, AND TIN[a]

Bismuth Amounts, mg		Antimony Amounts, mg		Tin Amounts, mg	
taken	error	taken	error	taken	error
105.0	-1.6	106.6	-0.5	129.3	-0.1
136.7	$+1.6$	192.6	-0.3	105.4	-0.7
61.4	$+3.7$	122.1	-2.9	169.0	-0.7[b]
121.8	$+2.3$	98.3	-2.1	101.9	-1.6
100.3	$+1.6$	108.3	-4.6[c]	104.5	-0.9
101.8	$+2.1$	200.1	-1.9	225.2	-1.8[d]

[a] $0.2M$ in citrate, pH 3.
[b] Tin tracer indicated 0.07% Sn in Sb, 1.0% left in solution.
[c] Sb tracer indicated 0.09% Sb in Bi, 3.3% in Sn.
[d] Sn tracer indicated 0.02% Sn in Bi, 0.03% in Sb.

Use of tracers demonstrated that deposits of bismuth from solution containing antimony and tin were essentially free of those elements, and that antimony was free of tin when deposited. However, the tin deposit sometimes contained antimony due to incomplete deposition of the latter. It is believed that antimony and tin deposits obtained after removal of bismuth were free of the latter because the combined weights of the latter were never significantly high.

A number of other electrolyte systems were investigated. The presence of suitable masking agent was found to be necessary. Bismuth and antimony could not be separated from simple acid systems as their aquo-ions. Electrodeposition from a $0.25M$ citrate, $0.1M$ Versene, sulfate system was less successful than from the simpler citrate-sulfate system. Results for bismuth were slightly high, and antimony results were invariably low. Generally unsatisfactory results were obtained when either a sulfate-tartrate or a sulfate-fluoride electrolyte was used. All the systems investigated, and the conclusions drawn therefrom, are summarized in Table II.

TABLE II

ELECTROLYTE SYSTEMS INVESTIGATED

System	Bi	Sb	Sn
HNO_3-citrate	Good	Low	Low
H_2SO_4-citrate	Sl. High	Good	Sl. Low
H_2SO_4-citrate-Versene	Sl. High	Low	—
H_2SO_4-tartrate	Good	Low	—
H_2SO_4-fluoride	Good	Low	—

PROCEDURE

The following procedure is recommended for the analysis of the single elements, or mixtures of the elements. Take a sample containing not over 100 mg of bismuth (if antimony is present in large amount), and not over 250 mg each of antimony and tin. Add 0.5 g of hydrazine sulfate and 10 ml of concentrated sulfuric acid. Heat without excessive boiling until all metal particles have disappeared. Allow the material to cool, and dilute with about 10-20 ml of water. Add 30 ml of 1*M* sodium citrate, 3 g of hydroxylamine or hydrazine sulfate, and neutralize to about pH 3 with 10*M* sodium hydroxide. Cool and dilute to 120-140 ml, and carefully adjust to pH 3.0 with sodium hydroxide or sulfuric acid, measuring the pH with a glass electrode-S.C.E. assembly. Heat to 70-80°, and deposit bismuth on a platinum gauze electrode, maintaining the reduction potential at —0.2 volt (S.C.E.) at first, then allowing it to rise to —0.3. Continue the electrolysis until the current falls to a small, constant value (usually requires about 25 min). Remove the electrode, washing with water from a wash bottle, agitate in two separate beakers of water, then in acetone. Dry in a stream of filtered air or by heating. Weigh and subtract 1.3 mg to obtain the weight of bismuth.

To the electrolyte add 1 g of hydrazine hydrochloride and 15 ml of hydrochloric acid. On a clean cathode, deposit antimony at 50-70° and at an initial current not exceeding 0.5 amp. Limit the potential to —0.3 volt, and continue electrolysis until the current falls to a small, constant value (usually requires about 30-45 min). Wash and dry the cathode as before. Determine the weight of antimony deposited.

Using a clean cathode, deposit tin at a potential of —0.6 volt, allowing it to rise to —0.65 volt after about 15 min (about an hour required). Remove the electrolyte by siphoning while diluting with water (about 400-500 ml). Finally siphon all liquid out, wash and dry the cathode as before. Weigh, adding 1.2 mg to obtain the weight of tin plated. The results should be accurate to about 1 mg. The total time required is about 3.5-4 hours. Copper deposits with bismuth, and lead with tin (if these metals are present).

SUMMARY

A study was made of the separation and determination of bismuth, antimony, and tin by electrochemical means, using controlled cathode potential. The effects of electrolyte composition, cathode potential, and temperature were investigated with respect to separations of the three metals and degree of recovery of each. Best results were obtained by use of an electrolyte containing sulfate and citrate. A procedure was devised which would serve for rapid analysis for bismuth, antimony and tin in the form of mixtures and alloys.

RÉSUMÉ

Les auteurs ont étudié la séparation et le dosage du bismuth, de l'antimoine et de l'étain, par électrolyse avec potentiel cathodique contrôlé. L'influence de la composition de l'électrolyte, du potentiel cathodique et de la température a été examinée en vue de la séparation et du dosage de ces 3 métaux. Les meilleurs résultats ont été obtenus avec un électrolyte formé de sulfate et de citrate. Un procédé est décrit pour effectuer un dosage rapide de bismuth, d'antimoine et d'étain dans un mélange ou sous forme d'alliages.

ZUSAMMENFASSUNG

Die Autoren haben die Trennung und die quantitative Bestimmung von Wismut, von Antimon und von Zinn durch Elektrolyse mit kontrollierten Kathodenpotentialen untersucht. Der Einfluss der Zusammensetzung der Elektrolyte, des Potentials der Kathode und der Temperatur wurde untersucht im Hinblick auf die Trennung und die Dosierung der drei Metalle. Die besten Resultate wurden mit einem Elektrolyten erhalten, der aus Sulfat und Citrat besteht. Es wird eine Methode beschrieben zur schnellen Bestimmung von Wismut, Antimon und Zinn in einem Gemisch oder in Legierungen.

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VERBESSERTE ENDPUNKTSBESTIMMUNG IN DER POTENTIOMETRISCHEN ANALYSE

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Es ist möglich, bei potentiometrischen Bestimmungen den Endpunkt auf etwa 1/50 des einzelnen Reagenszusatzes festzulegen und dies ohne graphische Auftragung irgend welcher Art, einfach durch Quotienten-Bildung aus zwei gemessenen Grössen. Was diese Vereinfachung einer wichtigen Arbeitsmethode für zahlreiche Zweige wissenschaftlicher und industrieller Untersuchung bedeutet, braucht nicht erklärt zu werden, dagegen erscheint es angebracht, die zum Verständnis nötigen Begriffe und Formelzeichen hier noch einmal kurz zusammenzufassen. (Vgl.[1,2]).

Wie jetzt allgemein anerkannt ist, muss gegen den Endpunkt einer potentiometrischen Titration das Reagens in stets unter einander gleichen Einzelmengen zugesetzt werden; diese ,,Volumenschritte" an Reagens bezeichnen wir mit Δv. Die einem Volumenschritt entsprechende Reagens-*Menge* ist durch Division in das Gesamtvolumen der titrierten Lösung als ***Konzentration*** auszudrücken und auf die ,,Kennkonzentration" der Titrierreaktion, c_0 zu beziehen, das ist die Konzentration, in der - infolge der Unvollständigkeit jeder Reaktion - die Reaktionspartner am Äquivalenzpunkt frei vorhanden sind; also bei einer Titration von Chlorid mit Silber: $C_{Cl^-} = C_{Ag^+} = 10^{-5}$; Jodid mit Silber: 10^{-8}; starke Base gegen starke Säure; $h = oh = 10^{-7}$, usw. Die Volumenschritte werden also als Vielfache von c_0 angegeben. Gleiche Reagensmengen oder Volumenschritte rufen bei Annäherung an den Endpunkt ständig wachsende Potentialänderungen oder ,,Potentialschritte", ΔE hervor; am Äquivalenzpunkt wird ein grösster Potentialschritt, Δ_m^E beobachtet, dann nehmen die Potentialschritte wieder ab. Den zweitgrössten der gemessenen Reihe bezeichnen wir mit Δ_1^E und den drittgrössten mit Δ_2^E unabhängig davon, welcher von ihnen vor und welcher nach Δ_m^E beobachtet wird. Aufgabe der Endpunkts-Interpolation ist es, zu ermitteln, um welchen Bruchteil ϱ des einzelnen Reagenszusatzes der richtige Endpunkt von dem zwischen Δ_m^E und Δ_1^E liegenden ,,Masspunkt" (zugegebenes Reagensvolumen) abliegt. Liegt in der Messreihe Δ_1^E vor Δ_m^E, so ist $\varrho\Delta v$ dem vor Δ_m^E liegenden Reagensvolumen zuzuzählen; liegt dagegen der zweitgrösste Potentialschritt vor dem grössten, so ist $\varrho\Delta v$ von dem dazwischen liegenden Reagensvolumen abzuziehen.

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Tabelle I gibt nun Potentialgänge, die für Reagenszusätze von 20 c_0 und ϱ-Werte von 0.5 bis 0.1 errechnet sind; ϱ wird aus diesen, in einzelnen Fällen zunächst angenähert als $\varrho_a = \Delta_2^E/2\,\Delta_1^E$ gefunden. Der Fehler dieser Berechnung, $\varrho_a - \varrho$, ist umso kleiner,* je näher ϱ an 0.5 liegt und je grösser Δ_m^E gegenüber Δ_1^E ist; für $\varrho_a \geqslant 0.25$ und $Q = \Delta_m^E/\Delta_1^E \geqslant 2.5$ ist $\varrho_a - \varrho < 0.02$; man sieht dies aus den Reihen 0.4 und 0.3 der Tabelle. Für die Reihe 0.2*a* ist $\varrho_a = 0.23$ und $Q = 2.4$; die Genauigkeit des ϱ-Wertes ist also zweifelhaft. Fasst man nun die Massteile paarweise zusammen (2 b), so wird ϱ_a fehlerfrei gleich $\varrho = 0.40$. In 0.1*a* ist $Q = 2.2$ und $\varrho_a = 0.21$; dies muss also ungenau sein; paarweise Zusammenfassung der Massteile (0.1b) macht $\varrho_a = 0.45$ fehlerfrei.

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* ϱ_a kann nicht kleiner gefunden werden als das wirkliche ϱ; wenn in der Tafel einmal der Wert 0.39 gegen 0.40 auftritt, so liegt das an einer Summierung von Kürzungsfehler in den pH-Werten (auf 2 Stellen gekürzte Logarithmen).

TABELLE I

Errechnete Potentialgänge für ein Gesamtvolumen der titrierten Lösung von etwa 100 ml und die angegebenen Reagenszusätze, $\triangle v$.

$\triangle v = 20\ c_0$. (Lit. 3).

$\triangle v$(ml)	normal	bei einer Titration von
0.02	0.001	Jodid gegen Silber
0.02	0.01	starke Säure gegen starke Base
0.2	0.1	Chlorid gegen Silber
0.4	0.1	Ammoniak gegen HCl oder Essigsäure gegen NaOH bei etwa halbnormalem Endprodukt.

Die Tabelle gibt $\triangle E = 100\ \triangle$ pH für die ϱ-Werte der Kopfspalte, zwischen

$v = n +$	0.5 ←ϱ→	0.4	0.3	0.2a	0.1a	0.0	1	0.2b	0.1b
$\triangle v$ 1	15	15	16	16	17	18			
2								43	45
	22	23	25	27	28	30			
3							3		
	47	54	63	75	95	130			
4								258	259
	201	199	184	183	164	130			
5							5		
	47	42	38	35	32	30			
6								54	50
	22	21	19	19	18	18			
7							7		
	15								
8									

Auswertung:

Reihen 0.5 und 0.0: ohne Rechnung ersichtlicht.

Reihe:	$Q =$	$\varrho_a =$
0.4	199/54 = 3.7	42/108 = 0.39; fehlerfrei (siehe Text).
0.3	184/63 = 2.9	38/126 = 0.30; fehlerfrei.
0.2a	183/75 = 2.4	35/150 = 0.23; vermutlich zu hoch.
0.1a	164/75 = 2.2	32/190 = 0.17; sicher zu hoch.
0.2b	258/54 = 4.8	43/108 = 0.40; fehlerfrei.
0.1b	239/50 = 5.2	45/100 = 0.45; fehlerfrei.

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ERRATA

Anal. Chim. Acta, Vol. 11 (1954).
p. 396, line 3 from bottom, last word "vor" should read "nach".

Praktisch ergibt sich danach folgende Arbeitsweise: Man wähle die Reagenszusätze etwa 20 mal so gross wie den zulässigen Fehler (also 1 ml, wenn die Bestimmung auf 0.05 ml genau werden soll). Liegt dann der Endpunkt günstig, so wird weniger als die Hälfte des zulässigen Fehlers begangen; liegt er aber ungünstig, so kann dem durch paarweises Zusammenfassen von Volumen- und Potentialschritten abgeholfen werden, und wir bleiben immer noch gut unter der zulässigen Fehlergrenze. Denn dieses Zusammenfassen macht aus der $\varrho = 0.1$ entsprechenden Endpunktslage $(0.1 + 0.9)\Delta v$ die Lage $(1.1 + 0.9)$, also $\varrho = 0.45$ (bezogen auf $2\Delta v$); aus $\varrho = 0.2$ wird im verdoppelten Massteil $\varrho = 0.40$ und aus $\varrho = 0.25$ wird $\varrho = 0.375$, sodass also hiermit stets ein für die Interpolation günstiger ϱ-Wert erreicht wird; damit dürfte die praktische Nützlichkeit des Verfahrens feststehen. Seine theoretischen Grundlagen sollen in einer ausführlichen Zusammenfassung des Gebietes gegeben werden ebenso ein graphisches Verfahren, das es gestattet, auch bei kleinsten Δv-Werten ϱa zum genauen Wert ϱ zu korrigieren, womit die grösste überhaupt mögliche Genauigkeit erreicht wird.

ZUSAMMENFASSUNG

Sind in einer potentiometrischen Titration die Reagenszusätze gleich $\triangle v$ und die gemessenen Potentialschritte, in abnehmender Grössenordnung, $\triangle^E_m$, $\triangle^E_1$ und $\triangle^E_2$ so findet man aus dem Quotienten $\varrho_a = \triangle^E_2 / 2 \triangle^E_1$ die Volumendifferenz $\varrho_a \triangle v$ zwischen dem Äquivalenzpunkt und dem bekannten Reagensvolumen. Der Endwert wird hiermit ausserordentlich genau bestimmt, und zugleich wird die Arbeitsweise wesentlich vereinfacht. Für $Q = \triangle^E_m / \triangle^E_1 < 2.5$ oder $\varrho_a < 0.25$ ist dieser Wert nur angenähert; aber in diesem Fall kann man aus den gemessenen Potentialschritten eine neue Serie mit doppelten Intervallen bilden, in der nun ϱ_a sehr nahe an 0.5 liegt; der Endpunkt wird somit völlig genau gefunden.

SUMMARY

If in a potentiometric titration each addition of reagent equals $\triangle v$ and if the observed potential steps are, in decreasing order, $\triangle^E_m$, $\triangle^E_1$ and $\triangle^E_2$, the ratio $\varrho_a = \triangle^E_2 / 2 \triangle^E_1$ is formed; $\varrho_a \triangle v$ is the difference between the equivalence point and the known volume of reagent next to it. Both an extraordinary increase in the precision and a valuable simplification of the analysis are obtained. For $Q = \triangle^E_m / \triangle^E_1 < 2.5$ or $\varrho_a < 0.25$ this value is approximated; but in this case a new series with doubled intervals may be formed from the potential steps observed in which ϱ_a is very near to 0.5, found hence absolutely accurate.

RÉSUMÉ

Si, lors d'une titration potentiométrique, chaque addition de réactif est égale à $\triangle v$ et si les variations de potentiel mesurées sont, par ordre décroissant, $\triangle^E_m$, $\triangle^E_1$ et $\triangle^E_2$, on obtient le quotient $\varrho_a = \triangle^E_2 / \triangle^E_1$. $\varrho_a \triangle v$ est alors la différence de volume du réactif entre le point d'équivalence et le volume connu le plus proche

de celui-ci. On obtient ainsi à la fois une augmentation extraordinaire de la précision du dosage et une simplification du mode opératoire. Lorsque $Q = \Delta^E_m / \Delta^E_1 < 2.5$ et $\varrho_a < 0.25$ cette valeur est approximative. Mais dans ce cas on peut former, en combinant les valeurs mesurées de deux en deux, une nouvelle série dans laquelle les intervalles sont doubles. ϱ_a est alors très proche de 0.5 et par conséquent très précis.

RESUMEN

Si en una titulación potenciométrica las cantidades de reactivo cada vez agregadas son Δv y las variaciones del potencial son, en orden decreciente, Δ^E_m, Δ^E_1 y Δ^E_2, se forma el cociente $\varrho_a = \Delta_2/2\Delta^E_1$; $\varrho_a \Delta v$ es entonces la diferencia de volumen que existe entre el punto de equivalencia y el volumen conocido más próximo a éste. Así se obtiene a la vez un incremento extraordinario de la precisión de la determinación y una simplificación notable en la manera de efectuarla. En el caso de $Q = \Delta^E_m / \Delta^E_1 < 2.5$ ó $\varrho_a < 0.25$, este valor es solamente aproximado; sin embargo, formando de las variaciones observadas una nueva serie, a intervalo doble, en ésta ϱ_a se halla muy cerca de 0.5 y se obtiene, por consiguiente, con precisión absoluta.

LITERATUR

[1] F. L. Hahn und M. Frommer, *Z. phys. Chem.*, 127 (1927) 1.

[2] Erich Müller, *Die elektrometrische (potentiometrische) Massanalyse*, Theodor Steinkopff, Dresden und Leipzig, 5. Aufl. (1932) S. 77.

[3] F. L. Hahn, *Anal. Chim. Acta*, 7 (1952) 203.

Eingegangen den 8. März 1954

p. 397, in Table I, line 2, for 100 ml read 20 ml.
in Table I, line 3, for $20\,c_0$ read $100\,c_0$.

REVUE DES LIVRES

Chromatography, A Review of Principles and Applications, par EDGAR LEDERER ET MICHAEL LEDERER, Elsevier Publishing Company, Amsterdam, 1953, xviii et 460 pages, 88 illustrations, 124 tableaux, plus de 2000 références, Dfl. 32,— (60s).

La chromatographie a subi un développement extraordinaire au cours de ces dernières années et le nombre des publications qui inondent la littérature est considérable. Si vaste est le domaine de la chromatographie qu'il est parfois difficile de s'y retrouver pour les non spécialistes et on peut être reconnaissant à MM. E. ET M. LEDERER d'avoir fait une remarquable synthèse des travaux effectués dans les multiples domaines de cette discipline.

Les divers sujets y sont exposés avec clarté, la lecture en est aisée et la présentation parfaite. On y trouve plus de deux mille références bibliographiques.

Cet ouvrage comprend plusieurs parties dont chacune d'elles est subdivisée en chapitres. Nous ne donnerons ici que ceux qui nous paraissent les plus importants:

1ère partie: *Adsorption Chromatographique:* modification de la technique de TSWETT, appareillage, adsorbants, solvants, constitution chimique et comportement chromatographique, chromatographie des substances incolores;

2ème partie: *Chromatographie par Echangeurs d'Ions:* résines synthétiques, équilibre théorique de la chromatographie par élution et comportement des composés organiques;

3ème partie: *Chromatographie par Partition*;

4ème partie: *Chromatographie de Substances Organiques:* hydrocarbures, alcools, phénols, aldéhydes etc., lipides, amino-acides, peptides, protéines, pigments naturels, vitamines, hormones, antibiotiques, séparation des stéréoisomères;

5ème partie: *Chromatographie des Substances Inorganiques:* adsorbants inorganiques, adsorbants organiques, séparation inorganique par échangeurs d'ions, séparation chromatographique des isotopes.

Nous ne pouvons donc que recommander chaudement cet ouvrage qui rendra les plus grands services aux spécialistes et à tous ceux qui veulent s'initier aux méthodes actuellement en usage et connaître les applications qu'on en a fait dans les domaines les plus variés.

D. MONNIER (Genève)

Gmelins Handbuch der Anorganischen Chemie, 8. Auflage, Verlag Chemie G.m.b.H. Weinheim/Bergstrasse, 1953.

Faisant suite à nos compte-rendus précédents (voir *Anal. Chim. Acta,* 4(1950) 108 et 324; 5(1951) 603; 7(1952) 481), nous avons le plaisir de signaler aujourd'hui à nos lecteurs la parution de 4 nouveaux volumes de cette remarquable encyclopédie:

9. Schwefel, Teil A, Lieferung 2. Vorkommen — Technologie des Schwefels und seiner Verbindungen — Kolloider Schwefel — Physiologische Schädigung. 450 pages, Kart. D.M. 244,—.

9. Schwefel, Teil A, Lieferung 3. Bildung und Darstellung — Das System Schwefel — Physikalische Eigenschaften — Elektrochemisches Verhalten — Chemisches Verhalten — Nichtwässrige Lösung — Schwefel als Lösungsmittel xvi + 252 pages, 54 Fig., D.M. 142,—.

9. Schwefel, Teil B, Lieferung 1. Hydride und Oxyde des Schwefels. xi + 372 pages, 75 Fig., D.M. 122,50.

10. Selen, Teil A, Lieferung 3. Selengleichrichter — Selenphotoelement. iv, xvii + 184 pages, 158 Fig., D.M. 111,—.

Y. RUSCONI (Genève)

THE DIELECTRIC CONSTANT AND SALT EFFECTS UPON THE ACID HYDROLYSIS OF ETHYL FORMATE*

by

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It was thought that the study of both the acid and basic hydrolysis of esters as a function of the dielectric constant of the solvent and of neutral salt concentration would be of interest in view of existing theories of rates of reactions between ions and dipolar molecules. Since esters are hydrolysed by both hydronium and hydroxyl ions the theories of ion-dipolar reaction rates could be investigated with respect to both positive and negative ions reacting with an identical dipolar molecule under like conditions of concentrations of reactants, temperature, and dielectric constant of solvent.

EXPERIMENTAL

The C. P. Ethyl Formate, Eastman Kodak is manufactured in a high state of purity and therefore the reagent was simply dried over burnt lime for 24 hours and then distilled at an atmospheric pressure of 725.5 mm of mercury. The fraction coming off between 52.1-52.2° C was collected. The density of ethyl formate was measured at 27° C and was found to be 0.89511 g/ml. Ethyl formate used in all kinetic runs was kept at 27° C and the required quantity of pure ethyl formate (0.414 ml) was added to the reaction solution at various temperatures. It was assumed that a negligible drop in the temperature of the reaction occurred.

The acetone was prepared according to the procedure of Akerlof[1] as follows: Acetone, J. T. Baker analyzed, was treated in batches of about three liters with a small amount of 85% bone phosphoric acid and immediately distilled. Then it was dried with burnt powdered lime for a day, poured off and redistilled; the fraction which came over between 55.5 and 56.0° C was collected. Weight per cent. of acetone for a kinetic run was calculated from the density determination of acetone at various temperatures.

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* This work was done on a contract made by the University of Arkansas with the Office of Naval Research.

Sodium nitrate, J. T. Baker analyzed; c.p. was used to prepare 1.0000*N* $NaNO_3$ stock solution; and this concentrated solution was then diluted to the required normality for various kinetic runs on salt effect.

Freshly boiled distilled water was always used in preparing solutions. A carbonate-free concentrated sodium hydroxide stock solution (about 0.4*N*) was prepared. The concentrated solution was then diluted and standardized against potassium biphthalate and stored in a paraffin-lined carboy. From this stock solution was prepared 0.0100*N* solution actually used in the kinetic runs.

A 0.4857*N* HCl stock solution was prepared by diluting c.p. concentrated (37%) acid and titrating against sodium carbonate. Then the 0.0200*N* HCl used in the runs was prepared as needed by dilution of the stock solution.

All volumetric apparatus and a set of analytical weights were calibrated and Bureau of Standard thermometers were used. The rate of hydrolysis was studied at temperatures of 35.01, 45.11 and 55.02° C. Insulated distilled water baths equipped with efficient stirring motors controlled the temperature within ± 0.01° C of the desired temperature.

Analytical techniques were checked by duplicating a kinetic run whose reaction velocity constant has been established. The acid hydrolysis of ethyl acetate as reported by HARNED AND PFANSTIEL[2] was selected for this purpose. Exact duplication of their experimental work gave very good checks of their reported velocity constants. This indicated that both the reagents and technique were satisfactory. No experimental results were available concerning the acid hydrolysis of ethyl formate.

The procedure to determine the kinetics of the acid hydrolysis of ethyl formate under conditions of varying (1) ionic strength, and (2) dielectric constant was as follows: Flasks containing the reagents were immersed in the thermostat and left for four hours for attainment of temperature equilibrium. Reaction was carried out in a calibrated volumetric flask. Concentrated solutions of reagents were prepared so that mixing them in the reaction flask and bringing the mixture to the volumetric mark by the addition of distilled water gave the desired concentration of each reagent. Duplicate runs were made in every case. The desired ionic strength was attained by adding the required amount of stock sodium nitrate solution. The addition of acetone in correct amounts gave the required dielectric constants for kinetic runs on the solvent effect. The reactions were followed by periodic withdrawals of 10.00 ml samples of the reacting mixture. The contents of the pipette were allowed to drain upon crushed ice prepared from distilled water to stop further hydrolysis of the ester. When the pipette was half empty the time was recorded. The cold samples, approximately 0.2° C, were then titrated with 0.0100*N* sodium hydroxide to a phenolphthalein end-point. The reactions were followed until hydrolysis was approximately 70% complete when possible. A final titration was made after the reaction had ample time to reach completion, usually several hours.

The reaction velocity constant, k', was calculated using the first-order equation

$$dx/dt = k' (a - x) \tag{1}$$

where dx/dt is the velocity of reaction,

a represents the initial concentration of ester
x the amount of ester changed in time t
k' the velocity constants of hydrolysis.

integrating equation (1)

$$k' = 1/t \ln a/(a - x) \tag{2}$$

Equation (2) expressed in terms of the number of milliliters of alkali employed in the titration becomes

$$k' = \frac{2.303}{t} \log (T_{\infty} - T_0)/(T_{\infty} - T) \tag{3}$$

where T_{∞} = Theoretical number of ml of alkali required for complete hydrolysis
T_0 = Initial titration; ml of alkali
T = Titration value at time t; ml of alkali
t = Time in minutes
k' = Specific velocity constant, min^{-1}.

It can be seen from equation (3) that a plot of log $(T_{\infty} - T_0)/(T_{\infty} - T)$ against t should give a straight line, and the specific velocity constant, k', can be calculated from the slope of the straight line. This was the method used in calculating most of the k' values. In some instances k' values were obtained by inserting titration and time values in equation (3).

The precision of the titrations and the agreement of the two methods of calculating k' are shown by the typical data in Table I.

TABLE I

DIELECTRIC DATA

Bath temperature 55.00 ± 0.02° C
Solvent 16.80% Acetone by Weight

Ethyl formate	0.0100M
HCl	0.0200M
NaOH	0.009627M

Time (min)	NaOH (ml)	T_{∞} -T	log T_{∞} -T	k'-10^2 (min^{-1})
0	20.75	10.39	1.0165	
9	23.60	7.54	0.8774	3.56
17	25.30	5.84	0.7664	3.39
24	26.30	4.84	0.6848	3.18
29	27.25	3.89	0.5899	3.39
38	28.30	2.84	0.4533	3.50
44	28.60	2.54	0.4048	3.20
50	29.20	1.94	0.2878	3.36
59	29.70	1.44	0.1584	3.35
68	30.10	1.14	0.0170	3.39
75	30.30	0.84	1.9243	3.35
∞	31.14		Average	3.36
			Graphical Result	3.40

Dielectric constant effect

In Table II are recorded the kinetic data at constant acid and ester concentration and constant ionic strength. In these data the dielectric constant decreases with increasing weight per cent acetone component of solvent. In addition to the specific velocity constant, k' the energies of activation and the ARRHENIUS frequency factors are included in Table II. The energies were calculated from the k'/C_{H_2O} values using the integrated ARRHENIUS equation which may be stated

$$\ln \frac{k'_2/(C_{H_2O})_2}{k'_1/(C_{H_2O})_1} = \frac{\Delta E}{R} \frac{(T_2 - T_1)}{T_2 \, T_1} \tag{4}$$

The frequency factor, B, was calculated using k'/C_{H_2O} values from an equation

$$B = \frac{T_2 \log (k'/C_{H_2O})_2 - T_1 \log (k'/C_{H_2O})_1}{T_2 - T_1} \tag{5}$$

The numerical value of these quantities are those observed in many instances for reactions in solutions.

In Fig. 1 is plotted log k' versus per cent. acetone by weight for the three temperatures, 35.01, 45.11 and 55.02° C. The specific velocity constant, k' decreases

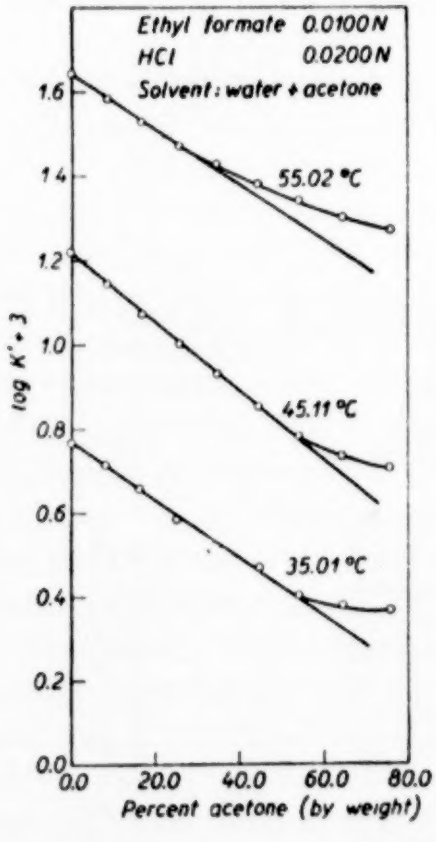


Fig. 1. Solvent effect on acid hydrolysis of ethyl formate.

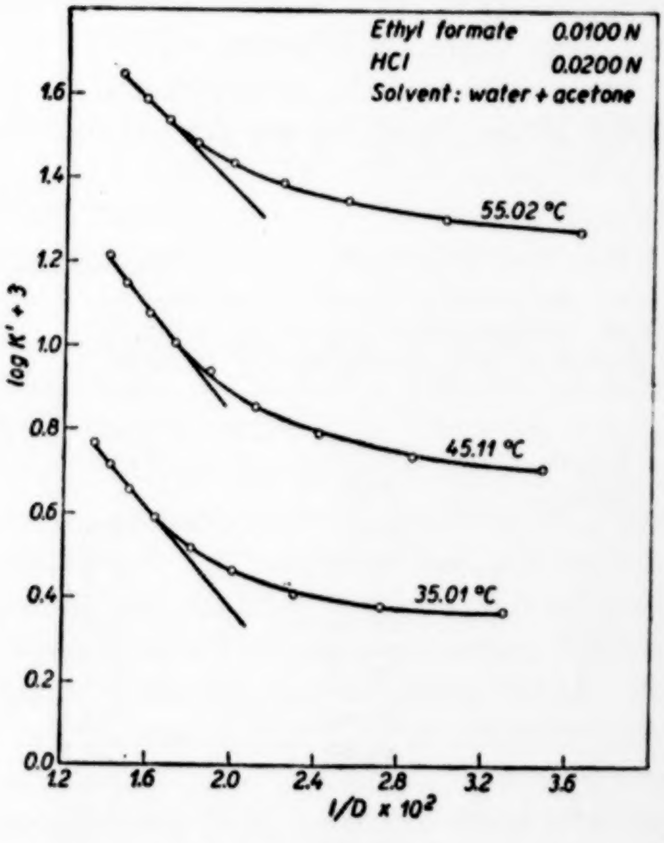


Fig. 2. Solvent effect on acid hydrolysis of ethyl formate.

TABLE II

EXPERIMENTAL VALUES OF VELOCITY CONSTANTS AS A FUNCTION OF DIELECTRIC CONSTANT; CORRESPONDING ENERGIES OF ACTIVATION AND FREQUENCY FACTORS

Ionic strength 0.0200 HCl 0.0200*M* Ethyl formate 0.0100*M*

Acetone % by wt.	D	$k'\cdot 10^3$ min^{-1}	$\frac{k'}{C_{H_2O}}\cdot 10^5$ l-min^{-1} mol^{-1}	$\triangle E$ (35.01—45.11) °C	B (35.01—45.11) °C
			Temperature 35.01° C		
0.0	74.82	5.85	10.64	20,100	10.29
8.4	70.47	5.16	10.43	19,200	9.64
16.8	66.07	4.47	10.17	18,900	9.40
25.4	60.95	3.85	10.01	18.700	9.24
34.5	55.34	3.30	10.01	18,500	9.17
44.1	49.55	2.90	10.55	17,700	9.57
54.0	43.35	2.55	11.60	17,200	9.21
64.6	36.73	2.38	14.4	16,100	8.59
75.7	30.34	2.30	20.9	15,200	8.13
			Temperature 45.11° C		
				(45.11—55.02) °C	(45.11—55.02) °C
0.0	71.20	16.5	29.9	20,800	10.78
8.4	66.99	13.9	28.5	21,400	11.15
16.8	62.37	11.8	26.8	22,200	11.66
25.4	58.08	10.05	26.1	22,900	12.14
34.5	52.97	8.55	25.9	24,000	12,90
44.1	47.10	7.20	26.2	25,500	13.90
54.0	41.50	6.15	28.0	26,600	14.75
64.6	34.99	5.45	33.1	26,700	12.42
75.7	28.71	5.03	45.7	26,800	18.90

Temperature 55.02° C

Acetone % by wt.	D	$k'\cdot 10^3$ min^{-1}	$k'/C_{H_2O}\cdot 10^5$ l-min^{-1} mol^{-1}
0.0	67.92	44.5	81.0
8.4	63.83	38.5	77.9
16.8	59.57	34.0	77.4
25.4	55.21	30.0	78.0
34.5	50.35	27.0	81.9
44.1	44.87	24.3	88.5
54.0	39.36	22.0	100.1
64.6	33.27	20.0	121.4
75.7	27.42	19.0	172.7

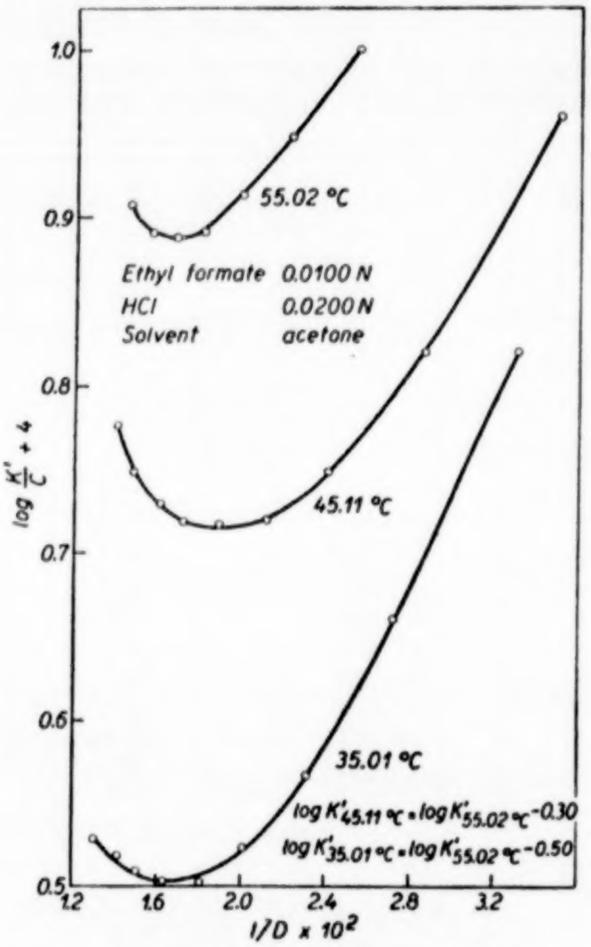
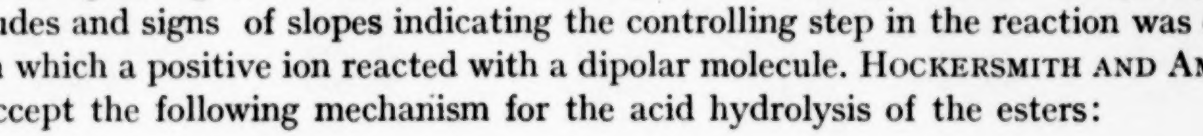


Fig. 3. Solvent effect on acid hydrolysis of ethyl formate.

with increasing concentration of acetone in a linear manner for all three temperatures except for the solutions containing higher percentages of acetone. The data at 55.02° C are observed to depart from linearity at a lower percentage of acetone than those at other temperatures.

In Fig. 2 is plotted log of specific velocity constant, k' versus the reciprocal of the dielectric constant of the medium. The specific velocity constant, k' decreases with decreasing dielectric constant showing a linear relationship in the region of higher dielectric constant. A departure from linearity was observed for all three temperatures at dielectric constant values between 55.5 to 58.8. These curves were similar to those of HOCKERSMITH AND AMIS[3] and NAIR AND AMIS[4].

In Fig. 3 is plotted log k'/C_{H_2O} against the reciprocal of dielectric constant of the medium for the three temperatures under investigation. HOCKERSMITH AND AMIS[3] and NAIR AND AMIS[4] plotted similar curves for the acid hydrolysis of methyl propionate and ethyl acetate respectively. The portions of their curves corresponding to higher value of dielectric constant were straight lines having magnitudes and signs of slopes indicating the controlling step in the reaction was one in which a positive ion reacted with a dipolar molecule. HOCKERSMITH AND AMIS[3] accept the following mechanism for the acid hydrolysis of the esters:



$$R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R' + H_3O^+ \rightleftharpoons \left[R\text{-}\overset{\overset{\displaystyle OH_2^+}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}\text{-}O\text{-}R' \rightleftharpoons R\text{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}\text{-}\overset{H}{\underset{+}{O}}\text{-}R' \right] \rightarrow R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OH + R'OH + H^+ \qquad (7)$$

They stipulate, however, that a step involving the product of the concentration of the positive ion and the concentration of dipole molecule governs the rate. No such conclusions can be drawn from the present data since log k'/C_{H_2O} first decreased, passed through a minimum, and then increased as the reciprocal of dielectric constant of the media increased at all three temperatures. The shapes of the curves are reminescent of catalytic catenaries. This suggests that the main influence of the solvent in the acid hydrolysis of ethyl formate is exerted upon the hydronium ion, and is effective by changing the activity of the ion.

The authors could find no electrostatic interpretation which was consistent with the data. However, the data for methyl propionate and ethyl acetate were explained on the basis of electrostatics. The dielectric constant data for acid hydrolysis of methyl propionate in acetone-water mixtures were well confirmed by electrostatic interpretation at all temperatures investigated. The data for ethyl acetate in acetone-water mixtures were progressively less amenable to electrostatics with increasing temperatures. Since data of ethyl acetate show some derivations from electrostatic requirements, extrapolation to the ester of formic acid might be expected to show more marked deviations.

Salt effect

In Table III are recorded the kinetic data when the solvent was water and ionic strength was changed with increasing concentration of neutral salt ($NaNO_3$). In Fig. 4 is plotted log k' against the negative logarithm of the activity of hydronium ion for three temperatures under investigation. The activity of hydronium ion was obtained by calculating activity coefficient, using the first approximation

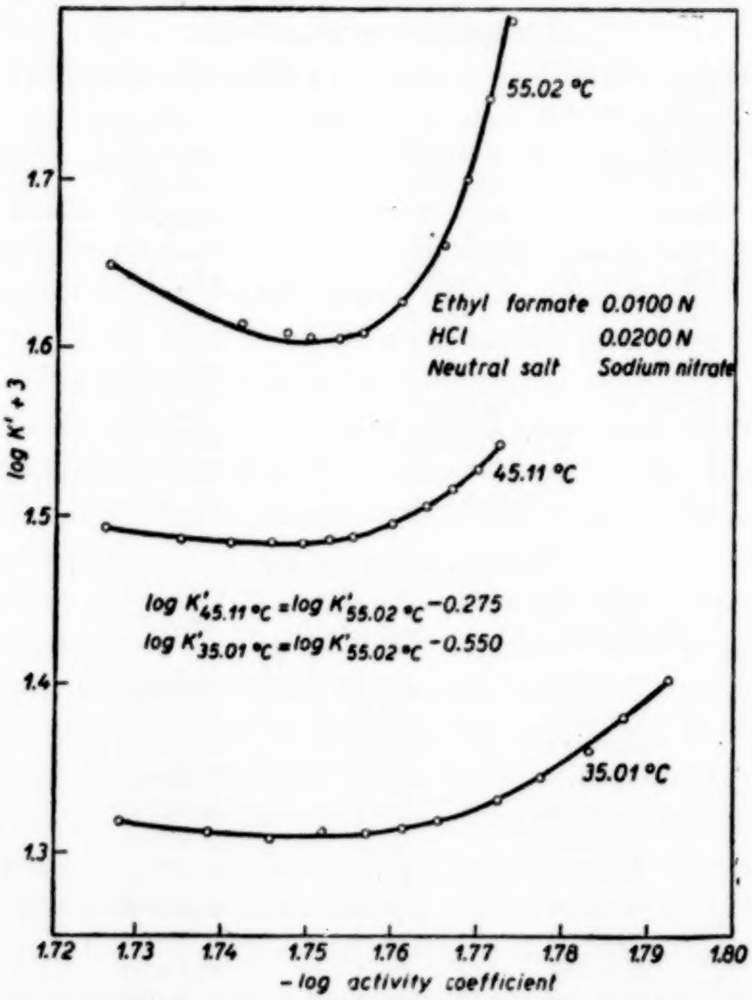


Fig. 4. Effect of neutral salt on acid hydrolysis of ethyl formate.

TABLE III

EXPERIMENTAL VALUES OF VELOCITY CONSTANTS AS A FUNCTION OF IONIC STRENGTH; CORRESPONDING ENERGIES OF ACTIVATION FREQUENCY FACTORS, AND ACTIVITY COEFFICIENTS

			Ethyl formate: 0.0100M	
D 74.82 Total ionic strength μ	$k' \cdot 10^2$ min^{-1}	HCl:0.0200M $f_{H_3O^+}$	ΔE (35.01—45.11) °C	B (35.01—45.11) °C
		Temperature 35.01° C		
0.0200	5.85	0.9356	20,100	12.03
0.0400	5.78	0.9133	20,100	12.03
0.0600	5.75	0.8976	20,000	12.00
0.0800	5.76	0.8853	20,000	11.95
0.1000	5.78	0.8752	19,900	11.92
0.1200	5.80	0.8664	19,900	12.03
0.1400	5.85	0.8586	19,900	11.90
0.1800	6.02	0.8453	19,700	11.78
0.2200	6.25	0.8341	19,400	11.57
0.2600	6.45	0.8243	19,300	11.50
0.3000	6.75	0.8166	18,900	11.25
0.3400	7.12	0.8087	18,500	11.00
		Temperature 45.11° C		
			(45.11—55.02) °C	(45.11—55.02) °C
0.0200	16.5	0.9396	20,800	12.41
0.0400	16.3	0.9206	19,900	11.85
0.0600	16.2	0.9080	19,500	11.50
0.0800	16.1	0.8984	19,300	11.33
0.1000	16.1	0.8908	19,100	11.20
0.1200	16.2	0.8843	19,000	11.17
0.1400	16.3	0.8784	19,000	11.19
0.1800	16.6	0.8691	19,500	11.53
0.2200	17.0	0.8611	20,700	12.34
0.2600	17.4	0.8549	22,200	13.36
0.3000	17.9	0.8494	23,800	14.50
0.3400	18.5	0.8445	25,400	15.60

Temperature 55.02° C

Total ionic strength (μ)	$k' \cdot 10^3$ min^{-1}	$f_{H_3O^+}$
0.0200	44.5	0.9383
0.0400	42.0	0.9356
0.0600	41.0	0.9063
0.0800	40.4	0.8969
0.1000	40.1	0.8888
0.1200	40.2	0.8820
0.1400	40.5	0.8764
0.1800	42.2	0.8668
0.2200	45.6	0.8570
0.2600	50.1	0.8525
0.3000	55.8	0.8468
0.3400	62.2	0.8419

of DEBYE-HUCKEL theory and the distance of closest approach from Fig. 2. The equation for this first approximation is

$$-\ln f_{\mathrm{H3O}^+} = \frac{Z^2_{\mathrm{H3O}^+}\, A\sqrt{\mu}}{1 + \beta\, a_i\sqrt{\mu}} \tag{8}$$

Where f_{H3O^+} is the activity coefficient of the hydronium ion of valence Z_{H3O^+} in a solution of ionic strength μ; A and β are the DEBYE-HUCKEL constants, which can be calculated from the known properties of the solvent and certain physical constants, and a_i is the distance of closest approach of two ions. Using the activity coefficients of hydronium ion and the concentrations of the hydrochloric acid, the activities of the hydronium ion in the various concentrations of reacting solutions could be found by multiplying the activity coefficient of the hydronium ion by its concentration. The concentration of the hydronium ion was assumed to be the same as the concentration of the acids. HOCKERSMITH AND AMIS[3] found that plots of log k' against the negative logarithms of the activity of the hydronium ion for methyl propionate were catalytic catenaries similar to those of Class B as classified by BELL[5].

In the class B catenaries the sides intersect at a sharp minimum with a slope of approximately 45 degrees with the horizontal. The catenaries obtained in the present investigation show a rounded minimum. The shapes of those catenaries are not similar to those of the ordinary classes of catenaries found in the literature. This data could not be explained on electrostatic theory from the standpoint of primary salt effect since if such was the case the positive-ion and neutral molecule mechanism should show an increase in the rate of reaction with increase in ionic strength. This is not the case as it could be seen from Fig. 5 where log of the specific velocity constant was plotted against ionic strength at the three temperatures investigated. These plots show an almost horizontal portion extending over half the ionic strength range before the rate constants increase with increase in ionic strength.

Both the dielectric constant dependence and the ionic strength dependence of the rate of acid hydrolysis of ethyl formate was found to diverge from the required electrostatic interpretation when a common solvent, acetone-water, is used at the three temperatures. How to explain the continual shift away from the electrostatic interpretation as one goes from methyl propionate, to ethyl acetate, to ethyl formate is not clear unless specific solvent effect becomes progressively larger. The decreasing size of the acid radical might be involved in the progressive departure of the data from the electrostatic theory, since in general, theoretical electrostatic relations are formulated to confirm data involving larger particles.

It is possible that removal of other alkyl carbon atoms from the carbonyl carbon might cause the direct field effect of this portion of the molecule to be more negative. This increased negativity of the carbonyl end of the ester molecule might account for the observed effect of dielectric constant upon the rate. NAIR AND AMIS[6] found that a carbon alpha to the carbonyl carbon when possessing two chlorine atoms gave curves of the logarithms of the termolecular hydrogen ion catalyzed hydrolysis constants versus $1/D$ values somewhat similar to the curves in Fig. 3 except that the left hand descending portions of the NAIR-AMIS curves were proportionally longer and were straight. NAIR AND AMIS[6] attribute this deviation from theory as possibly due to the increased negativity of the direct field effect of the chlorine substituted α-carbon.

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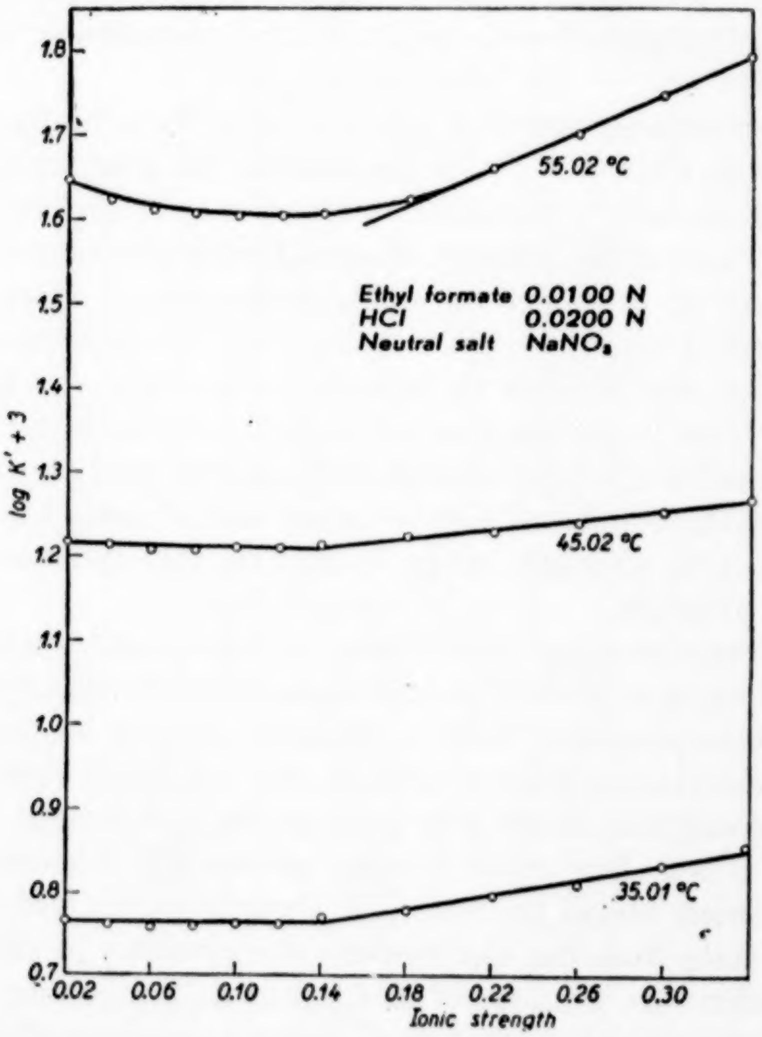

Fig. 5. Effect of neutral salt on acid hydrolysis of ethyl formate.

SUMMARY

The hydrolysis of ethyl formate catalysed by hydrochloric acid was studied at three temperatures in water-acetone media and in water media containing different concentrations of sodium nitrate. The effect of various ionic strengths and dielectric constants upon the rate of acid hydrolysis of ethyl formate is presented from the point of electrostatics and the results were compared to like effects upon the acid hydrolysis of ethyl acetate and methyl propionate. Neither the dielectric constant effect nor the salt effect lends itself readily to theoretical interpretation. It was assumed that a partial explanation of these anomalous results might be in the extrapolation of the acid radical to the simplest carboxylic acid. This suggestion was supported somewhat by the trends towards less adherance to the electrostatic theory at certain temperatures in the series methyl propionate, ethyl acetate and ethyl formate.

RÉSUMÉ

L'hydrolyse du formiate d'éthyle, catalysée par l'acide chlorhydrique, a été étudiée à trois températures différentes dans un milieu eau-acétone et dans un milieu eau-nitrate de sodium à diverses concentrations. L'influence des différentes forces ioniques et des constantes diélectriques sur la vitesse d'hydrolyse acide du formiate d'éthyle est étudiée du point de vue électrostatique et les résultats sont comparés à ceux obtenus lors de l'hydrolyse acide de l'acétate d'éthyle et du propionate de méthyle. Ni l'influence de la constante diélectrique, ni l'effet de sel ne peuvent conduire rapidement à des conclusions théoriques. Les résultats anormaux obtenus peuvent être dus en partie au passage du radical acide à l'acide carboxylique plus simple. Cette hypothèse est confirmée en quelque sotre par sa concordance moins grande avec la théorie électrostatique pour certaines températures dans les séries: propionate de méthyle, acétate d'éthyle et formiate d'éthyle.

ZUSAMMENFASSUNG

Die durch Salzsäure katalysierte Hydrolyse von Ethylformiat wurde untersucht bei drei verschiedenen Temperaturen in Wasser-Aceton und in Wasser, das Natriumnitrat in verschiedenen Konzentrationen enthält. Der Einfluss der verschiedenen Ionenstärken und der Dielektrizitätskonstanten auf die Geschwindigkeit der sauren Hydrolyse von Ethylformiat wurde in elektrostatischer Hinsicht untersucht und die Resultate wurden verglichen mit denjenigen, welche bei der sauren Hydrolyse von Ethylacetat und Methylpropionat erhalten wurden. Weder der Einfluss der Dielektrizitätskonstante noch der Salzeffekt kann schnell zu theoretischen Ableitungen führen. Die erhaltenen abnormalen Resultate können zum Teil durch den Übergang des sauren Radikals in die einfachere Carboxylsäure bedingt sein. Diese Hypothese wird in gewissem Masse bestätigt durch die geringere Übereinstimmung mit der elektrostatischen Theorie für gewisse Temperaturen in der Reihe: Methylpropionat, Ethylacetat und Ethylformiat.

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SODIUM META-VANADATE AS VOLUMETRIC REAGENT

II. IODINE MONOCHLORIDE METHOD

(Indirect Determinations)

by

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In the present investigation an attempt has been made to determine indirectly hydrogen peroxide, lead dioxide, manganese dioxide, selenium dioxide, potassium persulphate, copper sulphate, sodium formate and sodium sulphide by a volumetric method, using sodium meta-vanadate as an oxidizing agent.[1]

Sodium meta-vanadate is available in primary standard condition. Its solution is remarkably stable, especially when it contains about 0.1 per cent. of sodium carbonate. Advantages of the use of the iodine monochloride end-point in the titration of reducing substances with standard oxidizing solutions other than potassium iodate have been discussed by H. SWIFT[2]. The danger of loss of iodine, which is inherent when the conventional iodate reagent is used (because considerable amounts of iodine are liberated during the titration) is eliminated when only a small amount of iodine monochloride is added and another oxidizing agent is substituted for the iodate. No correction factor is needed either for the iodine monochloride added or the sensitivity of the end-point.

In all titrations with sodium meta-vanadate, 5 ml of $0.02M$ iodine monochloride, 5 ml of chloroform and sufficient hydrochloric acid to keep the normality between 7.0 and $7.5N$ were added to the titrant in a conical flask. Sodium meta-vanadate was added from a burette until the solution, which was coloured with iodine, became pale green. The conical flask was then stoppered and vigorously shaken. Addition of small volumes of the meta-vanadate solution was continued, shaking vigorously after each addition until the chloroform layer was faintly violet. The reagent was then added dropwise, with shaking after the addition of each drop, until the chloroform layer changed its colour from violet to light pale yellow. The end-point was very sharp.

Determination of hydrogen peroxide

A known amount of hydrogen peroxide was transferred to a conical flask and a known excess of arsenious oxide, dissolved in ten per cent. sodium hydroxide solution, was added to it. The mixture was allowed to stand for a couple of minutes and was acidified with concentrated hydrochloric acid. The excess of arsenious oxide, left unreacted in the mixture, was determined by titrating it against standard sodium meta-vanadate solution. The results are given in Table I.

TABLE I

HYDROGEN PEROXIDE

H_2O_2 taken g	$N/10$ As_2O_3 added ml	$N/10$ $NaVO_3$ used for excess As_2O_3 ml	$N/10$ As_2O_3 used by H_2O_2 ml	H_2O_2 found g
0.0187	20.00	9.00	11.00	0.0187
0.0243	25.00	10.75	14.25	0.0242
0.0318	27.00	8.40	18.60	0.0316
0.0374	30.00	8.10	21.90	0.0372

Determination of lead and manganese dioxides

A known amount of the dioxide was transferred to a conical flask and a known excess of potassium iodide solution was added to it. The excess of iodide was back-titrated with standard sodium meta-vanadate. The results are summarized in Tables II and III.

TABLE II

LEAD DIOXIDE

PbO_2 taken g	$M/20$ KI added ml	$N/10$ $NaVO_3$ used for excess KI ml	$M/20$ KI used by PbO_2 ml	PbO_2 found g
0.0860	15.00	7.80	7.20	0.0861
0.1316	20.00	9.00	11.00	0.1315
0.1824	25.00	9.70	15.30	0.1829
0.2322	30.00	10.50	19.50	0.2332

TABLE III

MANGANESE DIOXIDE

MnO_2 taken g	$M/20$ KI added ml	$N/10$ $NaVO_3$ used for excess KI ml	$M/20$ KI used by MnO_2 ml	MnO_2 found g
0.0320	15.00	7.50	7.50	0.0325
0.0425	20.00	10.30	9.70	0.0422
0.0480	25.00	14.00	11.00	0.0478
0.0848	30.00	10.55	19.45	0.0845

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Determination of selenium dioxide

A known weight of selenium dioxide was dissolved in a minimum quantity of hot water and a known excess of *M*/10 hydrazine sulphate solution was added to it. The mixture was heated to boiling. The selenium that separated was removed by filtration. The unused hydrazine sulphate in the filtrate was titrated against standard sodium meta-vanadate. The results are recorded in Table IV.

TABLE IV

SELENIUM DIOXIDE

SeO_2 taken g	*M*/10 $N_2H_4.H_2SO_4$ added ml	*N*/10 $NaVO_3$ used for excess $N_2H_4.H_2SO_4$ ml	*M*/10 $N_2H_4.H_2SO_4$ used by SeO_2 ml	SeO_2 found g
0.0888	10.50	10.00	8.00	0.0888
0.1110	12.50	10.00	10.00	0.1110
0.1660	19.00	16.00	15.00	0.1665
0.2040	23.00	18.40	18.40	0.2042

Determination of potassium persulphate

A known amount of potassium persulphate was transferred to a conical flask fitted with a Bunsen valve. Air in the flask was displaced by carbon dioxide. A known excess of *N*/10 ferrous ammonium sulphate solution and 25 ml of boiling water were poured into the flask, which was heated to mix the contents thoroughly. The flask was cooled by immersion in cold water and the excess of ferrous iron titrated against standard sodium meta-vanadate. The results are given in Table V.

TABLE V

POTASSIUM PERSULPHATE

$K_2S_2O_8$ taken g	*N*/10 $FeSO_4$.-$(NH_4)_2SO_4.6H_2O$ added ml	*N*/10 $NaVO_3$ used for excess $FeSO_4.(NH_4)_2SO_4.6H_2O$ ml	*N*/10 $FeSO_4.(NH_4)_2SO_4$-$6H_2O$ used by $K_2S_2O_8$ ml	$K_2S_2O_8$ found g
0.0866	15.00	8.60	6.40	0.0865
0.1318	20.00	10.25	9.75	0.1318
0.1934	30.00	15.70	14.30	0.1933
0.2800	40.00	19.30	20.70	0.2799

Determination of copper sulphate

A known weight of copper sulphate was dissolved in water and saturated with sulphur dioxide gas. The solution was boiled and a known excess of standard

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potassium thiocyanate was added to it. The precipitated cuprous thiocyanate was filtered. The filtrate was boiled in an atmosphere of CO_2 till free from sulphur dioxide gas, diluted with water to known volume and titrated against standard sodium meta-vanadate.

The results of the titrations are summarized in Table VI.

TABLE VI

COPPER SULPHATE

$CuSO_4 \cdot 5H_2O$ taken g	*M*/60 KCNS added ml	*N*/10 $NaVO_3$ used for excess KCNS ml	*M*/60 KCNS used by $CuSO_4 \cdot 5H_2O$ ml	$CuSO_4 \cdot 5H_2O$ found g
0.0499	25.00	13.50	11.95	0.0497
0.0603	30.00	15.40	14.60	0.0607
0.0832	35.00	15.10	19.90	0.0829
0.1248	40.00	10.00	30.00	0.1248

Determination of sodium formate

A known amount of sodium formate was transferred to a conical flask. Some sodium acetate solution, an excess of saturated mercuric chloride solution and sufficient water to bring the volume to about 75 ml were added to it. The mixture was heated on a steam bath for about two hours until no more carbon dioxide was evolved. The flask was cooled and the precipitated mercurous chloride was filtered. The precipitate along with the filter paper was transferred to a conical flask, and titrated against standard sodium meta-vanadate. The results are given in Table VII.

TABLE VII

SODIUM FORMATE

HCOONa taken g	*N*/10 $NaVO_3$ used ml	HCOONa found g
0.0272	8.00	0.0272
0.0357	10.50	0.0357
0.0510	15.00	0.0510
0.0680	20.10	0.0683

Determination of sodium sulphide

1.3 g of sodium sulphide were dissolved in 100 ml of water and the concentration of the solution was checked independently by iodometric titration. A known excess of arsenious oxide (2.3355 g) dissolved in sodium hydroxide was added. The mixture was thoroughly stirred and acidified with hydrochloric acid, when the yellow precipitate of arsenious sulphide was formed. The precipitate was filtered, washed with water and the filtrate made up to 250 ml. The excess of arsenious oxide present in the filtrate was determined by titrating it against standard sodium meta-vanadate. The results are tabulated in Table VIII.

TABLE VIII

SODIUM SULPHIDE

Na_2S taken g	Filtrate taken for titration ml	*N*/10 $NaVO_3$ used for As_2O_3 ml	As_2O_3 in 250 ml of filtrate g	As_2O_3 used by Na_2S g	Na_2S found g
	20.00	20.00			
1.3000	20.00	20.00	1.2365	1.0990	1.3000
	20.00	20.05			
	20.00	20.00			

From the results given in Tables I to VIII, it is evident that sodium meta-vanadate can be used as a volumetric reagent to determine indirectly hydrogen peroxide, lead dioxide, manganese dioxide, selenium dioxide, potassium persulphate, copper sulphate, sodium formate and sodium sulphide.

SUMMARY

Sodium meta-vanadate has been used as an oxidizing agent in hydrochloric acid medium for the indirect volumetric determination of hydrogen peroxide, lead dioxide, manganese dioxide, selenium dioxide, potassium persulphate, copper sulphate, sodium formate and sodium sulphide using iodine monochloride as a catalyst, pre-oxidizer and an indicator. Chloroform is coloured pink owing to the liberation of iodine during the titration and becomes light pale yellow at the end-point owing to the formation of iodine monochloride.

RÉSUMÉ

Le métavanadate de sodium peut être utilisé comme agent oxydant, en milieu acide chlorhydrique, pour le dosage volumétrique indirect du peroxyde d'hydrogène, du dioxyde de plomb, du dioxyde de manganèse, de l'anhydride sélénieux, du persulfate de potassium, du sulfate de cuivre, du formiate de sodium et du sulfure de sodium; on utilise alors le monochlorure d'iode comme catalyseur, préoxydant et indicateur. Le chloroforme se colore en violet par dissolution de l'iode libéré pendant la titration et il devient jaune pâle au point final par formation de monochlorure d'iode.

ZUSAMMENFASSUNG

Das Natriummetavanadat kann in salzsaurer Lösung als Oxydationsmittel verwendet werden für die indirekte volumetrische Bestimmung von Wasserstoffperoxyd, Bleibioxyd, Manganbioxyd, Anhydrid der selenigen Säure, Kaliumpersulfat, Kupfersulfat, Natriumformiat, Natriumsulfid. Dabei wird das Jodmonochlorid als Katalysator, präoxydierendes Mittel und Indikator verwendet. Das Chloroform wird violett gefärbt durch das aufgelöste Jod, welches während der Titration frei wird. Es wird hellgelb beim Endpunkt der Titration durch Bildung von Jodmonochlorid.

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CERATE OXIDIMETRY

I. OXIDATION OF FORMIC, GLYCOLIC, MALIC, MALONIC AND TARTARIC ACIDS

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The use of acidified solutions of ceric salts as volumetric reagent was suggested long ago by LANGE[1] and by JOB[2], but only in recent years have the applications of ceric salts been systematically studied by WILLARD AND YOUNG and by FURMAN and collaborators. In a recent review, PHILENA YOUNG[3] has given a critical summary of the work done so far.

In their study of the oxidation of various organic acids with potassium permanganate, HATCHER AND WEST[4] found that formic acid was an intermediate oxidation product. As pointed out by WILLARD AND YOUNG[5], the main difficulty in the determination of orgainc acids by potassium permanganate is due to the slow and variable oxidation of formic acid. BENRATH AND RULAND[6] had demonstrated that formic acid was not oxidized by ceric sulphate even on boiling. WILLARD AND YOUNG[5] confirmed the above observation of these workers and attempted to use the property in the controlled determination of organic acids. Thus, for example, tartaric acid would require six equivalents of oxygen per molecule if it were oxidized to formic acid only, but would require ten equivalents, if the oxidation was completed to carbon dioxide and water.

$$H_2C_4H_4O_6 + 3\ O \rightarrow 2\ H.COOH + 2\ CO_2 + H_2O$$
$$H_2C_4H_4O_6 + 5\ O \rightarrow 4\ CO_2 + 3\ H_2O.$$

However, in their actual determinations, WILLARD AND YOUNG[5] found that tartaric acid required 7.2 equivalents of oxygen per molecule under the specific conditions employed by them. Observations with other organic acids (glycolic, malic, and malonic) were similar to that with tartaric acid. WILLARD AND YOUNG[5], however, were able to devise emprical methods for the determination of these organic acids with ceric sulphate. In Table I a summary of their results is given and the fourth column clearly shows that the equivalents of oxygen consumed are intermediate between those given in the second and third columns. The last column summarizes the results achieved in this investigation and shows that in every case, the acid is oxidized completely to carbond ioxide and water by the recommended procedure:

TABLE I

Acid	Equivalents of O_2 reqd. if oxidized to HCOOH only	Equivalents of O_2 reqd. if oxidized completely to CO_2 & H_2O	Equivalents of O_2 used in the empirical method of WILLARD & YOUNG	Equivalents of O_2 used in the present method
Formic	—	2.00	very small oxidation	2.00
Tartaric	6.00	10.00	7.2	10.00
Malonic	6.00	8.00	6.66	8.00
Malic	8.00	12.00	9.25	12.00
Glycollic	4.00	6.00	3.95	6.00

WILLARD AND YOUNGS' work was repeated, and was confirmed in every case under their conditions. They, however, did not attempt to explain the above observations. If the organic acid decomposed via formic acid only, then the above observations suggest that although formic acid is not oxidized appreciably when present alone, yet its oxidation is induced by the energy evolved in the oxidation of other organic molecules. Preliminary observations confirming this probable view have been obtained and detailed results will be communicated elsewhere. Another plausible explanation might be that a portion of the organic acids is not oxidized via formic acid, but by some other mechanism in which its oxidation proceeds completely to carbon dioxide and water.

While confirming the non-oxidizability of formic acid by ceric sulphate, WILLARD AND YOUNG[5] pointed out, "that formic acid is not appreciably oxidized in hot acid solution by ceric sulphate, a result scarcely to be expected when one considers the ease with which it is oxidized by many oxidizing agents". In view of the extraordinary nature of the above reaction, it was considered worth while to re-investigate the oxidation of formic acid with ceric sulphate. On repeating the experiments of WILLARD AND YOUNG[5], it was confirmed that under the conditions employed by them, a slight amount of ceric sulphate was always consumed by formic acid, even when precautions were taken to avoid any extraneous source of error. This, however, led us to think that ceric sulphate is capable of oxidizing formic acid although the rate of oxidation is very slow. Contrary to the observation of BENRATH AND RULAND[6], it was found that an increase in the sulphuric acid concentration of the solution made the oxidation of formic acid more appreciable. This fact is very well demonstrated in Table II.

In a number of experiments 25 ml of ceric sulphate and different amounts of sulphuric acid were mixed, cooled, and 2 ml of formic acid (9.1816 g/litre) were added. The mixed solution was refluxed for one hour in every case. At the end, the excess of ceric sulphate was back titrated with standard ferrous ammonium sulphate. The results obtained are given in Table II.

TABLE II

0.0638N $Ce(SO_4)_2$ added ml	Conc.H_2SO_4 (Sp. gr. 1.82-84) added ml	$Ce(SO_4)_2$ consumed by the H.COOH ml	Percentage of formic acid oxidized
25	4	3.40	27.2
25	5	5.81	36.3
25	6	7.97	63.75
25	7	9.13	73.00
25	10	10.7	86.00
25	15	11.6	93.2
25	20	11.8	96.4
25	25	12.3	98.7

On varying the conditions, it was found that the oxidation of formic acid can be completed within 50 minutes in the presence of 66% (by volume) sulphuric acid in the reaction mixture.

Having established that formic acid is quantitatively oxidized by ceric sulphate, it was considered worth while to re-investigate the oxidation of the other organic acids employed by WILLARD AND YOUNG[5]. As shown in Table I, tartaric, malonic, malic and glycolic acids can be oxidized completely to carbon dioxide and water by the following general procedure.

The organic acid is mixed with a known excess of ceric sulphate and kept under reflux in a boiling water bath for ten to fifteen minutes. Concentrated sulphuric acid (66% of the total volume of the reaction mixture) is then added by inserting the pipette through the condenser, and heating in the water bath continued for another fifty minutes. At the end, the reaction mixture is diluted to about 200 ml and the excess of ceric sulphate is estimated by ferrous ammonium sulphate.

The above general procedure has been found to be the best after a large number of experiments. If concentrated sulphuric acid is employed from the beginning, the complete oxidation of organic acid requires a longer time in some cases. Similar observations have been made by BENRATH AND RULAND[6] who found that the oxidation of tartaric acid was made slower by the presence of sulphuric acid. Hence, it appears that in the recommended procedure, a major portion of the organic acid is oxidized to formic acid in the presence of dilute sulphuric acid in about ten minutes and then as indicated in Table II, the oxidation of formic acid is facilitated by the presence of concentrated sulphuric acid.

EXPERIMENTAL

Materials. Ceric sulphate employed was a Schuchardt product and was used without any further purification. Sulphuric acid was a refined quality of Bengal Chemical Works (Sp. gr. 1.82-1.84). Refluxing was carried out in an all glass apparatus with interchangeable joints, as the use of corks was found to affect the results.

Standardization. Ceric sulphate solution was standardized with standard oxalic acid (B.D.H. AnalaR) and by titrating against a standard solution of ferrous ammonium sulphate (B.D.H. AnalaR) using N-phenylanthranilic acid as indicator. The ferrous ammonium sulphate was standardized with standard potassium dichromate solution (B.D.H. AnalaR). The strength of the ferrous ammonium sulphate solution was determined against standard ceric sulphate daily before use.

Unless otherwise stated the ceric sulphate solution was prepared in 2*N* sulphuric acid.

FORMIC ACID

A solution (about 2%) of formic acid (Merck, purum quality) was prepared and its strength determined by titrating with alkaline potassium permanganate[7].

15 ml of ceric sulphate and 30 ml of concentrated sulphuric acid were mixed and cooled, 2 ml of formic acid solution was added and the solution refluxed on a water bath. At the end, the solution was diluted to about 200 ml and the excess of ceric sulphate titrated against standard ferrous ammonium sulphate using N-phenylanthranilic acid as indicator. The results obtained are given in Table III.

TABLE III

Time of Refluxing min	0.1005*N* $Ce(SO_4)_2$ ml	Conc. H_2SO_4 ml	$Ce(SO_4)_2$ consumed by H.COOH ml	Formic acid found g	Formic acid present g
10	15	30	3.33	0.007720	0.01837
21	15	30	5.31	0.01230	,,
30	15	30	6.64	0.01510	,,
40	15	30	7.40	0.01713	,,
50	15	30	7.94	0.01840	,,
60	15	30	7.94	0.01840	,,
90	15	30	7.94	0.01840	,,

In Table IV is given the effect of varying the concentration of ceric sulphate and formic acid, in the reaction mixture.

TABLE IV

Vol. of $Ce(SO_4)_2$ ml	Strength of $Ce(SO_4)_2$	Conc. H_2SO_4 ml	Time of refluxing min	$Ce(SO_4)_2$ consumed by HCOOH ml	Formic acid found g	Formic acid present g
25	0.0638*N*	50	50	12.46	0.01835	0.01837
15	0.09162*N*	30	50	8.700	0.01835	0.01837
5	0.1006*N*	10	50	2.51	0.00813	0.00813
5	0.1020*N*	10	50	3.11	0.00728	0.00728
5	0.1020*N*	10	50	2.50	0.00587	0.00587
5	0.1006*N*	10	50	2.11	0.00485	0.00488
5	0.1006*N*	10	50	1.71	0.00396	0.00396

TARTARIC ACID

MESTREZAT[8] studied the oxidation of tartaric acid by potassium permanganate and obtained an oxygen equivalent of 6.86. The oxidation was, later on, completed by alkaline permanganate. BENRATH AND RULAND[6] stated that the rate of oxidation of tartaric acid with ceric sulphate was retarded by the presence of sulphuric acid. WILLARD AND YOUNG[5] oxidized tartaric acid by ceric sulphate and obtained an oxygen equivalent of 7.2. However, by the general procedure described above, it is possible to oxidize tartaric acid completely to carbon dioxide and water.

Potassium acid tartrate (B.D.H. AnalaR) was used to prepare a standard solution of tartaric acid. Measured volumes of this solution were taken and mixed with ceric sulphate and refluxed according to the recommended general procedure. The results obtained are summarized in Table V.

TABLE V

$Ce(SO_4)_2$ 0.1005*N* ml	Tartaric acid soln. ml	Time of initial refluxing min	Conc. H_2SO_4 ml	Time of final refluxing min	$Ce(SO_4)_2$ consumed by the acid	Tartaric acid found g	Tartaric acid present g
10	1.0	15	20	50	6.75	0.01018	0.01021
10	1.0	8	20	50	6.75	0.01018	0.01021
20	2.0	10	40	50	13.53	0.02040	0.02041
20	2.5	10	40	50	16.93	0.02552	0.02551
10	1.0	10	10	75	6.75	0.01018	0.01021

When sulphuric acid was added at the very beginning of the reaction, the time required for complete oxidation of the organic acid was found to be much more than that required in the recommended procedure, in which case the sulphuric acid is added after an initial refluxing of 10-15 minutes.

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In Table VI are given the results obtained when sulphuric acid is added from very beginning.

TABLE VI

Tartaric acid soln. ml	0.1005N $Ce(SO_4)_2$ ml	Conc. H_2SO_4 ml	Refluxing time min	$Ce(SO_4)_2$ consumed by the tartaric acid ml	Tartaric acid found g	Tartaric acid present g
1.0	10.0	5.0	60	6.25	0.00939	0.01021
1.0	10.0	10.0	60	5.42	0.00814	,,
1.0	10.0	20.0	60	6.25	0.00939	,,
1.0	10.0	20.0	90	6.25	0.00985	,,
1.0	10.0	20.0	110	6.75	0.01018	,,
1.0	10.0	20.0	120	6.75	0.01018	,,
1.0	10.0	10.0	240	6.75	0.01018	,,
1.0	10.0	5.0	240	6.70	0.01006	,,

Oxidation of tartaric acid has also been studied at room temperature (25° C) and the results obtained are given in Table VII.

TABLE VII

Amt. of tartaric acid in 1 ml of soln. g	0.1006N $Ce(SO_4)_2$ (in 4N H_2SO_4) ml	Time for which allowed to stand at 25° C min	$Ce(SO_4)_2$ consumed by tartaric acid ml	Equivalents of O_2 used up per mole of tartaric acid
0.00497	5.0	10	1.01	3.09
Do	5.0	15	1.31	4.00
Do	5.0	30	1.83	5.59
Do	5.0	60	2.22	6.79

MALONIC ACID

In hot acid solution, malonic acid has been treated with potassium permanganate[1] when it was claimed to be oxidized to formic acid only:

$$H_2C_3H_2O_4 + 3\ O \rightarrow H.COOH + H_2O + 2\ CO_2$$

Later investigators[10] found the method to be very irregular owing to the appreciable oxidation of formic acid. WILLARD AND YOUNG[5] oxidized malonic acid with ceric sulphate and obtained an oxygen equivalent of 6.66 per molecule of the acid.

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A recrystallized sample of malonic acid (B.D.H.) was used to prepare a standard solution. This solution was further standardized as acid by titrating against standard *N*/20 caustic soda. The sample showed a percentage purity of 99.95%. A measured volume of this solution was treated with ceric sulphate as described in the case of tartaric acid. The results obtained are given in Table VIII.

TABLE VIII

Malonic acid soln.	0.1077*N* $Ce(SO_4)_2$	Time of initial refluxing	Conc. H_2SO_4	Time of final refluxing	$Ce(SO_4)_2$ consumed by malonic acid	Malonic acid found	Malonic acid present
ml	ml	min	ml	min	ml	g	g
2.0	15.0	15	30	50	11.66	0.01634	0.01640
2.0	15.0	7	30	50	11.66	0.01634	0.01640
2.0	15.0	2	30	50	11.66	0.01634	0.01640
1.0	10.0	5	20	50	5.34	0.00818	0.00820
1.0	10.0	10	20	50	5.34	0.00818	0.00820

Table IX shows the results obtained when 2 ml of the malonic acid solution and 20 ml of ceric sulphate are mixed with varying amounts of concentrated sulphuric acid from the beginning and then refluxed.

TABLE IX

Malonic acid soln.	0.1077*N* $Ce(SO_4)_2$	Conc. H_2SO_4	Refluxing time	$Ce(SO_4)_2$ consumed by malonic acid	Malonic acid found	Malonic acid present
ml	ml	ml	min	ml	g	g
2.0	20	20	35	9.52	0.01244	0.01640
2.0	20	20	60	11.66	0.01634	0.01640
2.0	20	5	30	8.99	0.01542	0.01640
2.0	20	5	45	11.37	0.01592	0.01640
2.0	20	5	60	11.66	0.01634	0.01640
2.0	20	5	85	11.66	0.01634	0.01640
2.0	20	40	60	11.66	0.01634	0.01640

A perusal of the data in Table IX shows that the time required for complete oxidation is nearly the same as that in the general recommended procedure (Table VIII). This appears to indicate that, contrary to the behaviour of tartaric acid, the rate of initial oxidation of malonic acid is not affected by sulphuric acid. However, it was found that the inital oxidation of malonic acid by ceric sulphate is very fast and is completed within a few minutes at room temperature (25° C). Refluxing the solution does not appear to affect the equivalents of oxygen consumed.

In Table X are given the comparative results for the initial oxidation of malonic acid at two different temperatures:

TABLE X

Amt. of malonic acid in the soln. taken g	0.1005N $Ce(SO_4)_2$ ml	$Ce(SO_4)_2$ used up by allowing to stand for 5 min at 25° C ml	$Ce(SO_4)_2$ used up by refluxing for 10-15 minutes ml	Equivalents of O_2 used up per mole of the acid
0.01012	15	6.45	—	6.67
0.01012	15	—	6.44	6.66
0.01012	10	6.44	—	6.66
0.01012	10	—	6.44	6.66
0.02024	25	12.90	—	6.66
0.02024	25	—	12.90	6.66

A comparative study of the data in Tables VII and X shows that the initial oxidation of malonic acid to formic acid is much faster than that of tartaric acid, and is completed within a very short time. Therefore, it is easy to understand why the addition of concentrated sulphuric acid from the beginning affects the time required for complete oxidation only in the case of tartaric acid.

MALIC ACID

MESTREZAT[8] oxidized malic acid by acidic permanganate and found an oxygen equivalent of 8.81 for the reaction:

$$H_2C_4H_4O_5 + 4\ O \rightarrow 2\ HCOOH + 2\ CO_2 + H_2O.$$

WILLARD AND YOUNG[5] studied the oxidation of malic acid by ceric sulphate in hot acid solution and got the oxygen equivalent of 9.25 for the same reaction. However, it is possible to oxidize malic acid completely to carbon dioxide and water by the general procedure recommended in the cases of tartaric and malonic acids.

Malic acid (B.D.H.) was purified by crystallization from acetone — carbon tetrachloride mixture, and a solution (about 1%) in water was prepared. The solution was standardized as acid by titrating against $N/20$ caustic soda solution and the sample showed a purity of 99.5%.

This solution of malic acid was treated with ceric sulphate in the same manner as given before for the other two acids, and the results obtained are tabulated in Table XI.

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TABLE XI

Malic acid soln. ml	0.1005N $Ce(SO_4)_2$ ml	Time of initial refluxing min	Conc. H_2SO_4 ml	Time of final refluxing min	$Ce(SO_4)_2$ consumed by malic acid ml	Malic acid found g	Malic acid present g
1.0	15	15	30	50	7.87	0.00883	0.00884
1.0	15	10	30	50	7.86	0.00883	0.00884
1.0	10	10	30	50	7.87	0.00883	0.00884
2.0	20	10	30	50	15.73	0.01767	0.01766

If the sulphuric acid is added from the beginning and refluxed directly the results shown in Table XII are obtained.

TABLE XII

Malic acid soln. ml	0.1005N $Ce(SO_4)_2$ ml	Conc. H_2SO_4 ml	Refluxing time min	$Ce(SO_4)_2$ consumed by the malic acid ml	Malic acid found g	Malic acid present g
1.0	15	5	60	7.84	0.00881	0.00883
1.0	15	5	90	7.87	0.00884	0.00883
1.0	15	10	60	7.87	0.00884	0.00883
1.0	15	10	90	7.87	0.00884	0.00883
1.0	15	15	60	7.87	0.00884	0.00883
1.0	15	15	90	7.87	0.00884	0.00883
1.0	15	15	120	7.87	0.00884	0.00883

TABLE XIII

Glycolic acid soln. ml	0.1005N $Ce(SO_4)_2$ ml	Time of initial refluxing min	Conc. H_2SO_4 ml	Time of final refluxing min	$Ce(SO_4)_2$ consumed by glycolic acid ml	Glycolic acid found g	Glycolic acid present g
2.0	10	20	20	50	3.72	0.00526	0.00526
2.0	10	15	20	50	3.72	0.00526	0.00526
4.0	10	15	20	50	7.44	0.01051	0.01052
5.0	15	15	30	50	9.33	0.01319	0.01320
10.0	25	15	50	50	18.66	0.05261	0.05262

GLYCOLIC ACID

WILLARD AND YOUNG[5] oxidized glycolic acid by ceric sulphate and found that 3.95 equivalents of oxygen are used up for the reaction.

$$H_2C_2H_2O_3 + 2\ O \rightarrow H.COOH + CO_2 + H_2O.$$

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Glycolic acid (B.D.H.) was used to prepare a standard solution which was standardized by alkaline permanganate[7].

Table XIII includes the results obtained by our general method described above.

If the concentrated sulphuric acid is added from the beginning, the time required for complete oxidation becomes greater as is shown by the data in Table XIV.

TABLE XIV

Glycolic acid soln. ml	0.1115N $Ce(SO_4)_2$ ml	Conc. H_2SO_4 ml	Refluxing time min	$Ce(SO_4)_2$ consumed by glycolic acid ml	Glycolic acid found g	Glycolic acid present g
2.0	10	10	150	3.64	0.00515	0.00526
2.0	10	10	180	3.72	0.00525	0.00526
2.0	10	10	240	3.72	0.00525	0.00526
5.0	20	20	180	9.33	0.01319	0.01320
5.0	25	25	180	9.33	0.01319	0.01320

SUMMARY

1. Contrary to the observations of earlier workers, it has been shown that formic acid can be quantitatively oxidized by ceric sulphate in the presence of concentrated sulphuric acid.

2. Tartaric, malonic, malic and glycolic acids can also be oxidized completely to carbon dioxide and water by the following general procedure: to a known amount of the organic acid is added ceric sulphate (excess) solution in dilute sulphuric acid and the mixed solution refluxed for ten to fifteen minutes. Concentrated sulphuric acid (double the volume of the reaction mixture) is then added taking care that formic acid is not lost during the addition, and the mixture again refluxed for 45 to 50 minutes. The excess ceric sulphate is determined by titrating against ferrous ammonium sulphate.

3. The complete oxidation of the above acids provides satisfactory methods for their quantitative estimation.

RÉSUMÉ

1. Contrairement aux observations de certains auteurs, il a été démontré que l'acide formique peut être oxydé quantitativement par le sulfate de cérium (IV), en présence d'acide sulfurique concentré.

2. Les acides tartrique, malonique, malique et glycolique peuvent aussi être oxydés quantitativement en anhydride carbonique et eau par le procédé général suivant: on ajoute à l'acide organique (en quantité connue) un excès de sulfate de cérium (IV) en solution dans de l'acide sulfurique dilué; puis on fait bouillir à reflux pendant 10 à 15 minutes. On verse ensuite dans ce mélange le double de son volume d'acide sulfurique concentré, il faut travailler avec précautions pour qu'il n'y ait pas de pertes d'acide formique. On chauffe de nouveau à reflux pendant 45 à 50 minutes. L'excès de sulfate cérique est titré par une solution de sulfate de fer(II) et d'ammonium.

3. L'oxydation de ces acides permet un dosage quantitatif et satisfaisant.

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ZUSAMMENFASSUNG

1. Entgegen den Beobachtungen gewisser Autoren wird gezeigt, dass die Ameisensäure quantitativ mit Cerium(IV) sulfat oxydiert werden kann in Gegenwart von konzentrierter Schwefelsäure.

2. Die Wein-, Malon-, Malin- und Glykolsäure können auch quantitativ oxydiert werden in Kohlendioxyd und Wasser durch das folgende Verfahren: zu der organischen Säure (in bekannter Quantität) gibt man einen Überschuss an Cerium(IV) sulfat, welches in verdünnter Schwefelsäure gelöst ist. Dann wird mit Rückflusskühler während 10 bis 15 Minuten zum Sieden erhitzt. Zu diesem Gemisch wird dann das doppelte Volumen konzentrierte Schwefelsäure gegossen. Man muss vorsichtig arbeiten, damit keine Verluste an Ameisensäure entstehen. Man erhitzt von neuem unter Rückflusskühlung während 45 bis 50 Minuten. Der Überschuss an Ceriumsulfat wird mit einer Eisen(II)-Ammoniumsulfat-Lösung titriert.

3. Die Oxydation dieser Säuren ermöglicht eine gute quantitative Bestimmung.

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SOME OBSERVATIONS ON THE DIMEDONE METHOD FOR THE GRAVIMETRIC DETERMINATION OF FORMALDEHYDE

by

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KOLTHOFF AND STENGER[1] describe a method for the determination of formaldehyde in aqueous solution in which 1,3,1′,3′-tetraketo-5,5,5′,5′-tetramethyl-4-4′-dicyclohexylmethane, the condensation product of formaldehyde and dimedone (5,5-dimethylcyclohexane-dione -1,3), is filtered and either weighed or estimated by alkali titration. However, they consider that the details as given by VORLANDER[2] and on which their method is based are inadequate, and that a further investigation is desirable.

A kinetic study of this reaction has been undertaken[3], the results of which will be published elsewhere. It has been found that the rate of this reaction is immeasurably slow in strongly acid solution, but increases to a maximum at pH 8.5, and that the product can be quantitatively precipitated from the reaction mixture by the addition of excess concentrated hydrochloric acid.

The variation with pH of the second order rate constant at 25°C is shown in Table I, whilst Table II shows the temperature dependence of the rate constant as obtained from measurements in $0.05M$ potassium hydrogen phthalate buffer solution which has a very small pH – temperature coefficient.

TABLE I

pH	k (2nd order) $\times 10^{-2}$	pH	k (2nd order) $\times 10^{-2}$
1.22	.0019	7.0	92.5
3.2	1.35	8.6	92
3.4	2.15	9.2	88
3.6	3.2	10.0	78
4.0	6.8	11.1	69
4.2	9.7	12.4	53
4.4	14.6	13.0	41
5.0	40.7	13.5	30
6.0	77	13.7	14

TABLE II

Temp. °C	Rate $k \times 10^{-2}$
25.0	6.0)
	6.3)
30.2	9.9)
	9.8)
36.4	18.1)
	18.1)
39.3	21.6)
	22.1)
45.3	34.6)
	36.0)

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These rate constants were calculated from the equations (1) and (2); hence by reference to Table I the time required for 99.9% precipitation at any pH can be calculated.

Thus, if *a* and *b* are initial concentrations of dimedone and formaldehyde respectively; and *x* is the amount of formaldehyde which has reacted in time *t*, then

$$k = \frac{2.303}{t\,(a/2-b)} \log_{10} \frac{2b}{a} \frac{(a/2 - x)}{(b - x)} \quad \ldots\ldots\ldots\ldots \quad (1)$$

For the special case when the initial molar concentration of dimedone is twice that of formaldehyde, *i.e.* $a = 2b$,

$$\text{then } k = \frac{1}{2t(b - x)} - \frac{1}{2tb} \quad \ldots\ldots\ldots\ldots \quad (2)$$

The results also show that whilst the observations of YOE AND REID[4] are substantially correct, a more satisfactory procedure involves an estimation at pH 8—8.5, in which solution the rate of condensation is of the order six times that at pH 4.6, the figure quoted by YOE AND REID. Such a procedure as that described below, gave satisfactory results in our work.

EXPERIMENTAL

Reagent solution. Dimedone in phosphate/citric acid buffer at pH 8.0[5].

Dissolve 0.80 g of dimedone in 15 ml of ethyl alcohol, and dilute to 1 litre with the buffer solution.

200 ml of such a solution will precipitate the formaldehyde from aqueous solutions in which the concentration does not exceed 15 mg in 50 ml.

Procedure. The reaction mixture, in volume not greater than 250 ml is allowed to stand at room temperature for 12 h (or at temperature up to 50°C to effect a further six-fold increase in reaction rate and so a correspondingly shorter reaction time of 2 h).

The reaction mixture is cooled to room temperature, strongly acidified with an excess, 25 ml, of concentrated hydrochloric acid. The precipitate is filtered through a previously weighed G3 sintered glass crucible, thoroughly washed with water, dried at 105-110 °C for 1 h, cooled and weighed.

292 mg of precipitate = 30 mg of formaldehyde.

SUMMARY

Tables are provided which give the dependence on the temperature and the pH of solution of the second order rate constant for the reaction between dimedone and formaldehyde.

These, together with the relevant rate equations, enable calculations to be made of the optimum conditions of analysis of formaldehyde solutions by the dimedone method.

RÉSUMÉ

Les auteurs ont étudié l'effet sur la température et sur le pH des vitesses de réaction du 2ème ordre entre la dimédone et le formaldéhyde.

Les tables établies, de même que les équations de vitesse applicables permettent de calculer les conditions optima du dosage de solutions de formaldéhyde au moyen de dimédone.

ZUSAMMENFASSUNG

Tabellen sind gegeben, welche die Abhängigkeit der Geschwindigkeitskonstante zweiter Ordnung der Reaktion zwischen Dimedon und Formaldehyd von der Temperatur und dem pH der Lösung zeigen.

Diese, zusammen mit den dazugehörigen Geschwindigkeitsgleichungen, ermöglichen die Berechnung der optima Zustände für die Analyse von Formaldehyd mittels der Dimedon Methode.

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FRACTIONNEUR AUTOMATIQUE À SIPHON
FORME ET CARACTÉRISTIQUES DES SIPHONS POUR LIQUIDES POLAIRES ET LIQUIDES NON-POLAIRES

par

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Pour les séparations chromatographiques sur colonne de gel de silice, de résine ou de poudre de cellulose à l'aide d'un fractionneur automatique à siphon, nous avons recherché la forme et les caractéristiques des siphons qui assurent le fractionnement le plus efficace. On peut estimer que celui-ci est efficace quand les volumes recueillis dans les tubes successifs sont identiques et quand il ne reste pas de liquide dans le siphon après écoulement, c'est-à-dire s'il n'y a pas mélange de liquide de deux fractions successives; cette deuxième condition n'est jamais réalisée d'une façon absolue.

Ecoulement et amorçage du siphon

L'obtention de volumes identiques dépend des conditions d'amorçage du siphon et de la manière dont s'effectue l'écoulement du liquide après l'amorçage.

Le but même du siphon est de substituer respectivement à un écoulement continu ou peu discontinu (écoulement par gouttes), un écoulement discontinu ou plus discontinu (écoulement par fractions de un ou de plusieurs ml). Or dans certains cas ce rôle n'est pas rempli, en particulier pour des débits d'alimentation trop grands par rapport à la durée de siphonage: pendant que le siphon se vide des quantités importantes de liquide continuent à être introduites, qui sont aussitôt aspirées elles aussi; on obtient un écoulement continu. Pour des débits un peu moins grands, le liquide qui est introduit vers la fin du siphonage est également aspiré, mais il ne s'écoule plus; il demeure dans le tube de sortie sous forme de colonnes de liquide séparées par des colonnes d'air; le siphon donne donc lieu à un écoulement très irrégulier d'une fraction à l'autre. Pour des débits encore moins grands, le liquide introduit au cours de l'écoulement n'est plus aspiré, mais le volume de ce liquide varie d'une fraction à l'autre et les fractions successives ont des volumes différents. Il convient donc d'opérer avec des débits d'alimentation suffisamment faibles, et il existe, pour un siphon donné, un débit qu'on ne peut dépasser. Pour des débits plus faibles on peut obtenir l'identité des volumes à condition que le nombre de gouttes introduites pendant la durée du siphonage soit toujours le même au cours des siphonages successifs. Il est donc

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important que le débit reste le plus possible constant au cours d'une séparation chromatographique.

Avec certains siphons on observe que, même pour des débits convenables, le solvant s'écoule goutte à goutte au fur et à mesure de l'arrivée de nouvelles gouttes dans le siphon. Cela tient à la constitution du coude supérieur: plus la tension superficielle du liquide est faible, plus le diamètre intérieur de ce coude doit être faible également; ainsi un siphon qui fonctionne correctement avec l'eau, peut produire un écoulement par gouttes avec le chloroforme ou le butanol. Mais quand on diminue le diamètre, la durée de siphonage augmente et les débits d'alimentation doivent être faibles. On peut ainsi être amené à utiliser pour des fractions de volume restreint (1 ml) des siphons particuliers[1] pour des solvants tels que l'eau, le chloroforme, l'éther, dont les tensions superficielles, respectivement de 72.8, 27 et 16.5 dynes/cm à la température de 20°, sont assez éloignées les unes des autres. Au cours d'une chromatographie la tension superficielle d'un mélange de solvants peut varier. Ainsi, dans la chromatographie des acides organiques sur colonne de gel de silice, la tension superficielle du mélange chloroforme-butanol varie légèrement; l'influence de cette variation est négligeable et on peut évidemment utiliser un seul et même siphon pendant toute la séparation.

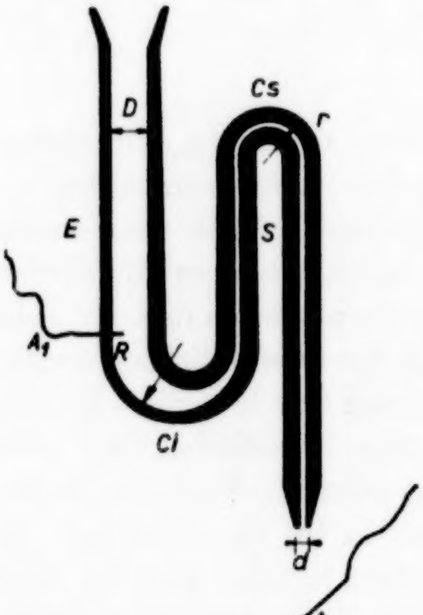

Fig. 1.

E : tube d'entrée
S : tube de sortie
Ci: coude inférieur
Cs: coude supérieur
R : rayon R de Ci
r : rayon r de Cs
D : diamètre de E
d : diamètre de S
A_1,A_2: électrodes

Par ailleurs, pour un diamètre donné, nous avons obtenu les meilleurs résultats lorsque le coude supérieur est isodiamétrique, de même diamètre que celui des autres parties du tube de sortie, et qu'il est demi-circulaire et de rayon suffisamment petit pour produire un amorçage rapide. La sensibilité à l'amorçage dépend surtout du diamètre intérieur du tube d'entrée: plus ce diamètre est petit, plus la quantité de liquide nécessaire à l'amorçage peut être faible pour un état de remplissage donné du siphon. Mais à capacité égale de ce dernier, la surface du tube mouillée par le liquide et, par conséquent le volume du liquide de mouillage augmentent en raison inverse du diamètre. Ce volume doit être aussi minime que possible afin d'avoir une bonne séparation; on est donc limité dans la réduction du diamètre du tube d'entrée.

La constitution du coude inférieur est aussi très importante. Schram et Bigwood[2] ont attiré l'attention sur la nécessité d'avoir un coude dont la lumière aille régulièrement en se retrécissant du tube d'entrée au tube de sortie. Les traces du coude sur une section longitudinale passant par les axes des tubes sont deux demi-circonférences de rayon différent et dont les centres sont décalés. Cette forme de coude évite, vers la fin du siphonage, d'une part l'entrée d'air dans le tube des sortie entre le liquide qui finit de s'écouler et, d'autre part l'aspiration des gouttes qui tombent dans le creux du coude quand le ménisque inférieur a déjà quitté le coude. Ces gouttes s'accumulent dans le creux, mais n'obstruent pas la lumière pour des débits d'alimentation convenables.

En tenant compte de ce qui précède, on peut obtenir des fractions successives dont les volumes sont identiques à 0.2% près pour un siphon de 3.5 ml environ fonctionnant avec du chloroforme, et à 0.05% pour un siphon de même capacité travaillant avec de l'eau.

Importance des liquides rémanents

Dans la totalité du liquide qui demeure dans le siphon immédiatement après siphonage, on peut distinguer:

1) le film liquide qui reste appliqué contre les parois,

2) le liquide de mouillage qui retombe le long des parois et qui s'accumule d'une part dans le coude inférieur et d'autre part au-dessus de la sortie du siphon,

3) le liquide qui éventuellement n'est pas siphoné de par la forme du coude inférieur et de par la tension superficielle faible du solvant employé,

4) le liquide à l'extrémité du tube de sortie, retenu par les forces capillaires; l'ensemble de ces quatre parties appartient à le fraction qui vient de s'écouler;

5) le liquide qui a été introduit pendant la durée du siphonage, qui commence à s'accumuler dans le coude inférieur et qui appartient à la fraction suivante.

— Le volume du film liquide est peu important par rapport aux volumes des autres liquides rémanents.

— Le volume du liquide qui retombe le long des parois varie approximativement comme l'inverse du diamètre. Pour un diamètre donné, ce volume augmente avec la vitesse d'écoulement du siphon. Pour des vitesses suffisamment faibles, ce liquide a le temps de retomber sur le ménisque et il est siphoné: à la limite on n'aurait à tenir compte que du volume du film liquide.

— Le liquide n'est pas totalement siphoné quand il est de faible tension superficielle, malgré la forme particulière du coude inférieur, dans le cas des siphons de capacité relativement grande, 3.5 ml environ. Cela tient à ce que vers la fin du siphonage le ménisque ne se déplace pas perpendiculairement aux parois du coude et reste plutôt près de l'horizontalité; aussi, se détache-t-il à un moment donné de la paroi supérieure du coude et l'air peut entrer; les dernières fractions de liquide qui s'écoulent aspirent de l'air au détriment du liquide qui persiste dans le creux du coude. On pourrait réduire le diamètre de ce dernier et se rapprocher des coudes isodiamétriques, mais alors on retombe dans le défaut mentionné plus haut, à savoir l'introduction d'air entre le liquide qui siphone. Le volume du liquide qui persiste ainsi est d'autant plus grand que l'écart entre les diamètres des deux tubes est plus important. Pour un siphon de 3.5 ml, le volume maximum de solvant qui s'accumule dans le coude en raison des divers facteurs envisagés est de 0.10 ml avec le chloroforme et de 0.03 ml avec l'eau. Pour des capacités plus petites (1 ml), les siphons qui conviennent au chloroforme fonctionnent mal avec l'eau : le diamètre du tube de sortie est alors trop faible pour la tension superficielle plus élevée de l'eau. On peut donc dire que les siphons de capacité relativement grande fonctionnent bien avec des liquides de tension superficielle assez grande et que ceux de petite contenance donnent de bons résultats avec des solvants de tension superficielle assez faible.

— Le liquide qui obstrue la sortie du siphon est minimum pour une extrémité du tube limée en forme de tronc de cône. D'ailleurs quand le siphon se remplit à nouveau, l'air emprisonné dans le tube de sortie est soumis à une pression croissante et finit par chasser le liquide hors du tube sous forme de quelques gouttelettes; si le fractionneur n'a pas tourné jusque là, ces gouttes retombent dans la fraction dont elles proviennent; sinon elles s'écoulent dans le tube suivant, ce qu'il faut éviter si possible. Il est donc avantageux d'avoir des fractionneurs qui ne tournent qu'après la tombée de ces gouttes.

Siphons pour liquides polaires et liquides non-polaires

Le fractionneur que nous utilisons est constitué essentiellement d'un plateau circulaire qui porte les tubes et dont la rotation est commandée par la fermeture d'un circuit électrique. Pour les liquides polaires ou faiblement polaires, le circuit est fermé à travers le liquide lui-même par l'intermédiaire de deux électrodes en platine, au moment du siphonage. La Fig. 1 représente la forme des siphons qui, pour des solvants conducteurs de tension superficielle faible ou élevée, nous a donné les meilleurs résultats, compte tenu des facteurs envisagés plus haut, et dont voici les caractéristiques:

	Capacité de 1 ml	Capacité de 3.5 ml
Diamètre D	6 mm	8 mm
Diamètre d	1 mm à 1.5 mm	2 mm
Rayon R	10 mm	13 mm
Rayon r	6 mm	8 mm

Ces siphons sont ceux qui conviennent aux solvants de tension superficielle assez élevée, et pour lesquels le volume du liquide rémanent est minimum quand on utilise des solvants de faible tension superficielle.

Dans le cas des liquides non-polaires, nous avons obtenu la fermeture du circuit électrique au moyen d'un flotteur constitué d'une sphère de verre soufflé, surmontée d'un fil de platine de 0.4 mm de diamètre et long de 40 mm (Fig. 2). Il coulisse par l'intermédiaire du fil de platine dans un manchon de laiton relié au circuit. Le but de ce manchon est de faire arriver dans le fil de platine le courant

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électrique et de guider le flotteur dans l'axe du tube. Une borne qui constitue la deuxième extrémité du circuit ouvert est disposée au-dessus du tube d'entrée du siphon. A un certain niveau du liquide, le fil de platine butte contre la borne et ferme le circuit. Pour que ce dispositif soit utilisable en toute sécurité, il faut que le contact se fasse à chaque siphonage et que le fractionnement reste efficace au sens où nous l'avons défini précédemment.

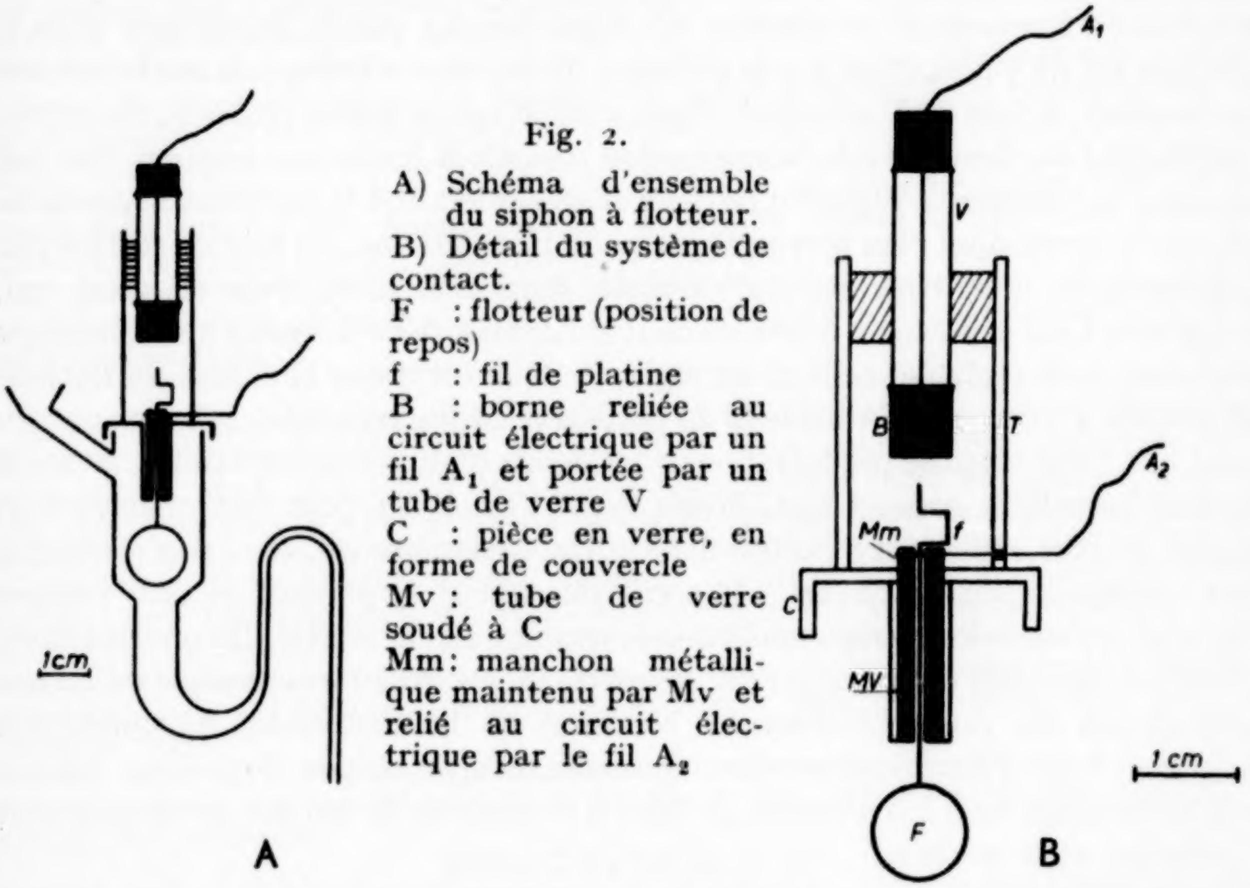

Fig. 2.

A) Schéma d'ensemble du siphon à flotteur.
B) Détail du système de contact.
F : flotteur (position de repos)
f : fil de platine
B : borne reliée au circuit électrique par un fil A_1 et portée par un tube de verre V
C : pièce en verre, en forme de couvercle
Mv : tube de verre soudé à C
Mm: manchon métallique maintenu par Mv et relié au circuit électrique par le fil A_2

Le flotteur doit être aussi léger que possible; le calcul et l'expérience ont montré que la sphère doit avoir un diamètre de 10 mm pour assurer un bon maintien du flotteur à la surface du liquide; son poids total est alors de 350 à 400 mg environ. De manière à ce que le flotteur se déplace fidèlement avec le niveau du liquide, il faut éviter qu'il touche les parois du tube: le diamètre de celui-ci doit être suffisamment grand, et le fil de platine dans le manchon doit posséder le jeu minimum compatible avec un bon coulissage. D'autre part, pour que l'amorçage reste régulier, il ne faut pas que la périphérie du ménisque au centre duquel se trouve le flotteur, soit perturbée. Il convient donc d'élargir suffisamment le haut du tube, mais, afin que l'amorçage reste sensible, on ne peut dépasser un certain diamètre. Nous avons choisi finalement un tube de 18 mm de diamètre intérieur; il semble assez difficile de descendre en dessous de cette valeur, à moins de diminuer le rayon de la sphère, mais alors la poussée d'Archimède devient trop faible par rapport au poids du flotteur qui reste sensiblement le même. On pourrait encore utiliser un fil d'un métal de densité plus petite que celle du platine, mais alors il y aurait risque de corrosion. Aussi nous semble-t-il que la contenance du siphon de capacité minimum que l'on peut construire d'après ces données avec les moyens habituels des laboratoires, est de 2 à 2.5 ml environ.

Une pièce en verre en forme de couvercle, traversée en son centre par un tube de verre, est destinée à maintenir le manchon métallique dans l'axe principal du siphon. Quand le siphon est vide, le flotteur reste suspendu à cette pièce grâce à un coude en forme de U plié dans le fil de platine. La course du flotteur dans le manchon est de 5 mm. Afin que le présence du flotteur n'influe pas sur le volume des fractions, il faut qu'il occupe à chaque amorçage la même position. On arrive à ce résultat en donnant à la borne contre laquelle il butte une hauteur fixe par rapport à la position de repos du flotteur et en conférant à la surface inférieure de la borne la forme d'un plan perpendiculaire au fil de platine. La borne est fixée par l'intermédiaire d'un bouchon par exemple, dans l'axe d'un tube de verre qui, en appuyant sur la pièce en forme de couvercle, maintient la borne à une hauteur constante, mais réglable; celle-ci est réglée de telle sorte que la course du flotteur soit réduite à 3 ou 4 mm. Ainsi le fil de platine vient butter contre la borne un peu avant que l'amorçage se produise; pour des débits d'alimentation faibles, la durée pendant laquelle le contact reste établi avant l'amorçage peut être relativement longue. De plus, si on veut recueillir dans la fraction même qui vient de s'écouler le petit volume de liquide retenu à la sortie du siphon, le plateau ne doit tourner d'un cran qu'assez longtemps après que le contact ait été établi. Il convient donc d'avoir un dispositif électronique qui permette un retard à l'avancement suffisamment grand. M. SORCINA (Institut National de la Recherche Agronomique. Versailles) nous a fourni un système de commande au moyen duquel on dispose de retards allant de 0 à 6 minutes, et dont il se propose de publier prochainement le principe et le schéma.

Les conclusions dégagées de l'étude des siphons en général s'appliquent aux siphons à flotteur. Par exemple, il est essentiel qu'au tube de 18 mm fasse suite le tube de 8 mm de diamètre utilisé dans le siphon de 3.5 ml dont les caractéristiques ont été indiquées plus haut.

CONCLUSION

L'étude des siphons pour liquides polaires nous a permis de mettre au point un siphon à flotteur pour liquides non-polaires. Ces siphons à flotteur nous ont donné satisfaction. Ils rendent possible l'utilisation des fractionneurs automatiques à siphon dans le cas de solvants non-conducteurs. Ils peuvent aussi être utilisés avec les solvants conducteurs; ils permettent d'éviter alors le passage du courant électrique à travers le solvant. Ils délivrent des volumes successifs identiques à 0.5% près, à condition que les débits d'alimentation soient suffisamment faibles et constants au cours d'une séparation chromatographique. Leur réalisation *

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* Constructeur: CONSTANT BOOM, souffleur de verre, 14, rue Saint Charles, Paris 15.

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pratique est très simple; leur simplicité et leur fonctionnement fidèle et précis nous les font préférer aux siphons à mercure.

Nous nous faisons un plaisir de remercier Monsieur R. RAVEUX et Monsieur H. BOITEUX pour les conseils dont ils ont bien voulu nous faire profiter.

RÉSUMÉ

Nous avons recherché d'abord la forme, les caractéristiques et les conditions de fonctionnement des siphons qui assurent le fractionnement le plus efficace au moyen des fractionneurs automatiques à siphon. Les débits d'alimentation doivent être suffisamment faibles. Pour des solvants de tension superficielle peu élevée, le diamètre intérieur du coude supérieur ne doit pas dépasser une certaine valeur. Il est essentiel que la lumière du coude inférieur aille régulièrement en se rétrécissant du tube d'entrée au tube de sortie. Le volume du liquide qui demeure dans le siphon immédiatement après siphonage est minimum pour un diamètre déterminé du tube d'entrée et du tube de sortie, et pour un rayon adéquat du coude inférieur. Le bon fonctionnement du siphon dépend de l'équilibre entre ces divers facteurs qui jouent souvent en sens inverse l'un de l'autre.

A partir de ces données, nous avons ensuite réalisé un siphon à flotteur qui permet l'emploi de liquides non-polaires avec les fractionneurs automatiques à commande électrique.

SUMMARY

The shape, characteristics and conditions of working of the syphons that ensure the most efficient fractionating by means of automatic fraction collectors have been investigated. The liquid deliveries to the syphon must be sufficiently slow. With solvents having a low surface tension, the inside diameter of the upper elbow must not be greater than a given value. It is essential that the inside diameter of the lower elbow should become regularly narrower from the inlet tube to the outlet tube. The volume of the liquid remaining in the syphon immediately after draining is smallest for a given diameter of the inlet tube and of the outlet tube, and for a proper radius of the lower elbow. The good working of the syphon depends upon the balance between those various factors that often come into play in opposite ways.

Then, from these data, a syphon has been made equipped with a ball float that makes possible the use of non-polar liquids in the automatic fraction collectors electrically controlled.

ZUSAMMENFASSUNG

Es wurde zunächst versucht die Form, die Kennzeichen und die Arbeitsbedingungen derjenigen Siphonen festzustellen, die mittels eines automatischen Kollektors die wirksamste Zerteilung ermöglichen. Der Flüssigkeitszulass in das Siphon muss zur genüge schwach sein. Mit Flüssigkeiten niedriger Oberflächenspannung darf der Innendurchmesser des oberen Bogens einen bestimmten Wert nicht überschreiten. Es ist wichtig, dass der Innendurchmesser des unteren Bogens regelmässig vom Zugangsrohre bis zum Ableitungsrohre abnimmt. Die Flüssigkeitsmenge, die sofort nach Beendigung eines Saugausflusses im Siphon festgestellt werden kann, ist minimal für einen bestimmten Durchmesser des Zugangs- und des Ableitungsrohres, und für einen entsprechenden Halbmesser des unteren Bogens. Die in Betracht zu ziehenden Faktoren können entgegengesetzte Wirkungen haben; die Leistungen des Siphones hängen davon ab, wie der Ausgleich unter ihnen erreicht werden kann.

Nach diesen Angaben wurde dann ein Siphon mit Flösser ausgeführt, der es gestattet unpolare Flüssigkeiten mit einem elektrisch betriebenen Kollektor zu gebrauchen.

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DIE PHOTOMETRISCHE BESTIMMUNG DES WISMUTS MIT BROMWASSERSTOFFSÄURE

von

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EINLEITUNG

Bei der systematischen Überprüfung der Färbungen die von Metallen beim Zusammentreffen mit Bromwasserstoffsäure gebildet werden, haben wir festgestellt, dass Wismut(III)bromid mit Bromwasserstoffsäure einen Komplex bildet, der photometrisch zu einer Wismutbestimmung herangezogen werden kann. Die Möglichkeiten, die die Bromwasserstoffsäure zur Bestimmung von Eisen[1], Kupfer[2,5,6], Zinn[3] und Antimon[4] bietet sind von uns schon früher beschrieben worden.

VERSUCHE UND VERSUCHSERGEBNISSE

Reagenzien

Alle bei den nachfolgend beschriebenen Versuchen benutzten Reagenzien waren, soweit eine Abweichung nicht angegeben ist, Präparate pro Analysi der Firma Merck, Darmstadt oder Riedel de Haën, Seelze. Die zur Anwendung gekommene Bromwasserstoffsäure war von chemisch reinster Qualität und war in einer Glasschliffapparatur fraktionierend destilliert worden und nur die völlig farblosen Fraktionen wurden für die Versuche benutzt.

Apparatur

Die optischen Messungen zur Ermittlung der Durchlässigkeitskurve des Wismut(III)bromides in Bromwasserstoffsäure wurden mit einem Spektralphotometer mit Monochromator Type M4Q der Firma Carl Zeiss, Oberkochen ausgeführt. Die Untersuchung der Versuchseinflüsse und die Ausarbeitung des beschriebenen photometrischen Bestimmungsverfahrens geschah mit Hilfe filterphotometrischer Messungen im Gerät Elko-II der Firma Carl Zeiss, Oberkochen. Dieses Gerät gestattet die Durchlässigkeitswerte der Lösungen nach einer Substitutionsmethode sehr genau zu messen. Das Gerät Elko-II wurde hierbei mit dem Quecksilberbrenner, UV-Kondensor II und Filter S38E benutzt. Um die Versuchseinflüsse sicher und sehr genau zu erfassen, wurde unter Ausnutzung der vollen möglichen

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[*] Jetzt: Riedel de Haën Aktiengesellschaft Chemische Fabriken, Seelze/Hannover.

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Messgenauigkeit des Gerätes Elko-II an der Durchlässigkeitsskala sorgfältig die Ablesung vorgenommen. Auf eine an sich zulässige Mittelwertbildung aus vielen Messwerten konnte verzichtet werden, da die Streuung der Messungen mit dem Gerät Elko-II so gering ist, dass eine Verkleinerung der zufälligen Fehler der Einzelmesswerte durch Mittelwertbildung sich als nicht notwendig erwies. Sämtliche verwendeten Volumen-Messgefässe waren amtlich geeicht.

Ausserdem blieb die Arbeitstemperatur immer nahe bei 20° C, doch fand kein Thermostat Verwendung.

Wismutstammlösung

100.0 mg Wismut wurden in 20 ml 48%iger Bromwasserstoffsäure unter Zutropfen von Brom gelöst und nach Verkochen des Broms auf 100 ml mit Bromwasserstoffsäure 48% aufgefüllt. Diese Stammlösung I enthält 1 mg Wismut pro ml 48-%iger Bromwasserstoffsäure. Von dieser Wismutstammlösung wurden 10 ml abpipettiert und in einem 100 ml Messkolben mit Bromwasserstoffsäure 48% zur Marke aufgefüllt. Diese Wismutlösung II enthält 100 μg Wismut pro ml 48-%iger Bromwasserstoffsäure.

Durchlässigkeitskurve des Wismut(III)bromides in 48%iger Bromwasserstoffsäure aufgenommen mit dem Spektralphotometer

Zur Messung kam eine Wismut(III)bromidlösung 10 (μg/ml); in 48%iger Bromwasserstoffsäure die im Gerät Elko-II unter den schon beschriebenen Messbedingungen einen Extinktionsmodul von etwa 0.56 cm^{-1} zeigte. Diese Lösung wurde in Quarzküvetten im Spektralphotometer MQ4 der Firma Carl

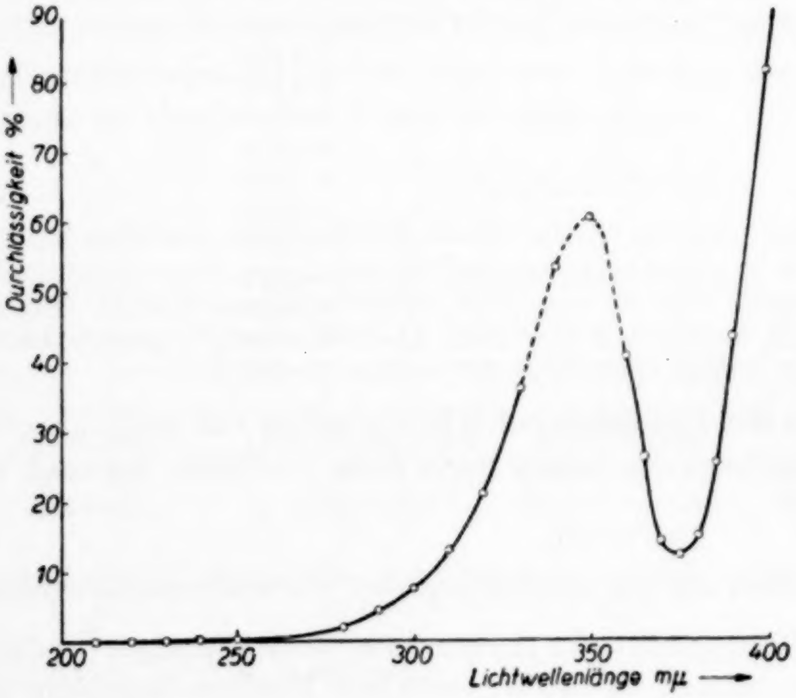

Fig. 1. Durchlässigkeitskurve von Wismut in Bromwasserstoffsäure. 10 μg Bi/ml, Schichtdicke 1.000 cm gegen eine Blindlösung mit Bromwasserstoffsäure (aber ohne Wismut) gemessen mit Spektralphotometer M4Q der Firma Carl Zeiss, Oberkochen.

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Zeiss, Oberkochen gemessen. Abb. 1 gibt das Resultat dieser Messungen grafisch wieder. Man ersieht aus dieser Abbildung, dass im Bereich von 370 bis 380 mμ ein zur Messung geeignetes Minimum in der Durchlässigkeitskurve vorhanden ist. Auf Grund dieses Befundes haben wir die filterphotometrischen Messungen im Gerät Elko-II in Verbindung mit dem UV-Kondensor II, Filter S38E und Quecksilberbrenner ausgeführt, da hierbei die monochromatische Lichtstrahlung der Quecksilberliniengruppe bei 366 mμ wirksam ist und somit mit genügender Annäherung im Bereich der höchsten Extinktionswerte gemessen wird.

Abhängigkeit der Extinktion des Wismut(III)bromidkomplexes von der Konzentration der Bromwasserstoffsäure

5 ml der Wismutstammlösung II wurden in einen 50 ml Messkolben gegeben und jeweils mit Bromwasserstoffsäure verschiedener Konzentrationen zur Marke aufgefüllt. In gleicher Weise, aber ohne Wismutzugabe wurde immer eine entsprechende Blindlösung hergestellt und diese als Kompensationsküvettenfüllung bei der Messung benützt. Das Ergebnis dieser Versuche ist in der Tabelle I wiedergegeben.

TABELLE I

ABHÄNGIGKEIT DER EXTINKTION DES WISMUT(III)BROMIDKOMPLEXES VON DER KONZENTRATION DER BROMWASSERSTOFFSÄURE

Messbedingung: Gerät Elko-II mit UV-Kondensor II, Quecksilberbrenner, Filter S38E in 100 cm Küvetten gegen eine Blindlösung. Wismutkonzentration 10 μg pro ml Lösung.

Prozentgehalt der Bromwasserstoffsäure zum Auffüllen	dek. Extinktionsmodul cm^{-1}
48.0	0.5599
40.1	0.5597
35.5	0.5600
30.1	0.5599
25.6	0.5597
20.4	0.5599
19.0	0.5400
15.5	0.4549
10.3	0.2650
5.7	0.0000

Man ersieht, dass die Farbe der Lösungen bei HBr-Gehalten von mehr als etwa 20% von der HBr-Konzentration, die sofort nach dem Auffüllen beendet ist, unabhängig ist.

Einfluss von Chlorwasserstoffsäure auf die Ausbildung des Wismutbromidkomplexes

Da das Bestimmungsverfahren praktische Anwendung in der Analyse Verwendung finden sollte, schien es ratsam zu prüfen, welchen Einfluss Salzsäure auf

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den Komplex ausüben kann, da bei vielen analytischen Aufgaben gerne mit Salzsäure gearbeitet wird. Hierzu wurde wie folgt vorgegangen.

5 ml der Wismutstammlösung II wurden in einen 50 ml Messkolben gegeben und mit steigenden Mengen an konzentrierter Salzsäure versetzt. Die zur Anwendung gekommenen Mengen und das Ergebnis dieser Versuche ist in der Tabelle II wiedergegeben. Anschliessend wurde der Kolben mit Bromwasserstoffsäure 48% zur Marke aufgefüllt.

TABELLE II

EINFLUSS VON CHLORWASSERSTOFFSÄURE AUF DIE AUSBILDUNG DES WISMUTBROMID-KOMPLEXES

Messbedingung: Gerät Elko-II mit UV-Kondensor II, Quecksilberbrenner, Filter S38E in 100 cm Küvetten gegen eine Blindlösung. Wismutkonzentration 10 µg pro ml Lösung.

ml Salzsäure conc. zugegeben	dek. Extinktionsmodul cm^{-1}
0	0.5599
1	0.4917
2	0.3278
5	0.2798

Wie man aus den vorstehenden Ergebnissen ersieht, darf Salzsäure in den Bestimmungslösungen nicht anwesend sein.

Erfüllung des Lambert-Beer'schen Gesetzes und Aufstellen einer Eichkurve

Um den Geltungsbereich des LAMBERT-BEER'schen Gesetzes für die Wismutbestimmung nachzuprüfen wurden Lösungen wechselnder Konzentration in verschiedenen Schichtdicken im Gerät Elko-II gemessen aus. Aus diesen Messungen wurde dann der Extinktionskoeffizient berechnet, sodass alle Messwerte hierdurch vergleichbar werden. In den folgenden Tabellen sind die Versuche und ihre Ergebnisse in abgekürzter Form wiedergegeben.

TABELLE III

ERFÜLLUNG DES LAMBERT-BEER'SCHEN GESETZES UND AUFSTELLUNG EINER EICHKURVE

Verschiedene Mengen der Wismutstammlösung I wurden in den 50 ml Kolben und mit Bromwasserstoffsäure 20% zur Marke aufgefüllt.

Messbedingung: Gerät Elko-II mit UV-Kondensor II, Quecksilberbrenner, Filter S38E in 0.100 cm Küvetten gegen eine Blindlösung.

µg/Wismut pro ml Lösung	Durchlässigkeit in % abgelesen	Extinktion berechnet für die 0.100 cm Küvette	dek. Extinktionsmodul cm^{-1}	Extinktionskoeff. $\mathrm{cm}^{-1}/(\mu g\ \mathrm{Bi/ml})$
40	59.00	0.2292	2.292	0.05730
80	36.55	0.4371	4.371	0.05763
120	23.45	0.6299	6.299	0.05250

TABELLE IV

Verschiedene Mengen von der Wismutlösung II wurden in 50 ml Kolben gegeben und mit Bromwasserstoffsäure 20% zur Marke aufgefüllt.
Messbedingung: Gerät Elko-II mit UV-Kondensor II, Quecksilberbrenner, Filter S38E in 1.000 cm Küvetten gegen eine Blindlösung.

μg Wismut pro ml Lösung	Durchlässigkeit in % abgelesen	dek. Extinktions-modul cm^{-1}	Extinktionskoeff. cm^{-1}/(μg Bi/ml)
2.0	77.27	0.1120	0.05600
4.0	59.70	0.2240	0.05600
6.0	46.14	0.3359	0.05599
8.0	35.64	0.4481	0.05601
10.0	27.54	0.5600	0.05600
12.0	21.28	0.6720	0.05600
14.0	16.45	0.7038	0.05600

TABELLE V

10.000 ml von der Wismutlösung II wurden in einen 100 ml Kolben gegeben und mit Bromwasserstoffsäure 48% zur Marke aufgefüllt. Diese Wismutlösung III enthält 10.0 μg Wismut pro ml Lösung.

Steigende Mengen der Wismutlösung III wurde in einen 50 ml Messkolben gegeben und mit Bromwasserstoffsäure 20%ig bis zur Marke aufgefüllt.
Messbedingung: Gerät Elko-II mit UV-Kondensor II, Quecksilberbrenner, Filter S38E in 5.000 cm Küvetten gegen eine Blindlösung.

μg Wismut pro ml Lösung	Durchlässigkeit in % abgelesen	Extinktion berechnet für die 5.000 cm Küvette	Extinktions-modul. cm^{-1}	Extinktions-koeffizient cm^{-1}/(μg Bi/ml)
1.0	52.48	0.2800	0.05600	0.05600
2.0	27.54	0.5600	0.11200	0.05600
3.0	14.45	0.8401	0.16802	0.05600

Wie das Ergebnis der in den Tabellen III bis V wiedergegebenen Messungen beweist ist das LAMBERT-BEER'sche Gesetz in einem Konzentrationsbereich von 1 bis 14 μg Wismut pro ml Lösung in 20%iger Bromwasserstoffsäure sehr streng erfüllt, sodass man geradlinige Eichkurven in diesem Bereich erhält. Bei höheren Konzentrationen von 40 bis 80 μg Wismut pro ml zeigen sich geringe Abweichungen vom BEER'schen Gesetz sodass man zweckmässig mit Eichkurven arbeitet die eine geringe Krümmung zeigen. Bei Konzentrationen oberhalb 80 μg Wismut pro ml ist eine Bestimmung auf photometrischem Wege auch noch möglich, doch sind hier die Eichkurven schon stärker gekrümmt.

Zeitabhängigkeit der Extinktion des Wismut(V)bromidkomplexes in Bromwasserstoffsäure

In besonderen Versuchen wurde festgestellt, dass der Komplex sofort nach dem Auffüllen konstante Extinktionswerte liefert und die Extinktion sich im Laufe der Zeit nicht ändert.

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Temperatureinfluss auf die Extinktion des Wismut(V)bromidkomplexes in Bromwasserstoffsäure

In weiteren Versuchen kamen Lösungen mit 4.0 µg Bi/ml und 10.0 µg Bi/ml mit HBr 20% aufgefüllt gegen Blindlösungen mit der gleichen Bromwasserstoffsäurekonzentration aber ohne Wismutzusatz bei verschiedenen Temperaturen zwischen 15 bis 30° C zur Durchlässigkeitsmessung. Es wurde hierbei festgestellt, dass die Temperatur keinen Einfluss auf die Ausbildung der Extinktion im genannten Bereich ausübt. Dieses Ergebnis darf sicher darauf zurückgeführt werden, dass praktisch im Extinktionsmaximum gemessen wird, wobei in der Regel Temperatureinflüsse sich am wenigsten bemerkbar machen.

ZUSAMMENFASSUNG

Auf Grund spektralphotometrischer Messungen wird gezeigt, dass Wismut in 20%iger Bromwasserstoffsäure im Bereich von 370 bis 380 mµ ein Absorptionsmaximum besitz, das zur filterphotometrischen Bestimmung mit Hilfe des Gerätes Elko-II, UV-Kondensor II, Filter S38E und dem Quecksilberbrenner herangezogen werden kann. Das LAMBERT-BEERsche Gesetz ist in einem Bereich von 1 bis 15 µg Wismut/ml streng erfüllt. Mit Hilfe von Eichkurven lassen sich noch Wismutkonzentrationen bis zu etwa 100 µg pro ml/Wismut photometrisch bestimmen. Die Extinktion des Wismut(III)bromids in 20%iger Bromwasserstoffsäure ist sofort konstant und im Temperaturbereich von 15 bis 30° C Temperatur unempfindlich.

SUMMARY

By means of spectrophotometric measurements, a method has been established for the determination of bismuth in 20% hydrobromic acid solution, at maximum absorption of 370 — 380 mµ.

An Elko-II apparatus is used with condenser UV II, filter S38E and a mercury lamp. The LAMBERT-BEER law is followed for strengths of 1 — 15 µg Bi/ml. Using a calibration curve, it is possible to determine up to 100 µg/ml.

The extinction of bismuth tribromide immediately attains a constant value, it does not vary between 15 and 30° C.

RÉSUMÉ

Des mesures spectrophotométriques ont permis d'établir une méthode de dosage du bismuth en solution dans l'acide bromhydrique à 20%, au maximum d'absorption de 370 — 380 mµ. On utilise un appareil Elko-II avec condenseur UV II, filtre S38E et lampe à mercure. La loi de LAMBERT-BEER est suivie pour des teneurs allant de 1 à 15 µg Bi/ml. Si l'on utilise une courbe d'étalonnage, il est possible de doser jusqu'à 100 µg/ml. L'extinction du bromure de bismuth(III) atteint tout de suite une valeur constante, elle ne varie pas entre 15 et 30° C.

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PHOTOMETRIC DETERMINATION OF TRACES OF ANTIMONY WITH RHODAMINE B AFTER SULFIDE PRECIPITATION

by

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In recent years photometric methods have been described for the determination of minute amounts of antimony in germanium[1], alloys[2], and bio materials[3]. All these make use of rhodamine B[4], which appears to be the most sensitive antimony reagent known at present. The procedure described below was worked out with silicate rocks particularly in mind. When the method was applied to igneous rocks, the average amount of antimony present was found to lie near the limit of detectability (0.1 p.p.m. for 1 g sample). However, the method can be used for shales (some of which may contain as much as a few p.p.m. of antimony) and for other sedimentary materials in which antimony occurs in amounts larger than in igneous rocks. Besides, it should be of general use when traces of antimony are to be determined in the presence of much iron, aluminum, and other common elements (atomic numbers 1-28).

The method adopted for the separation of antimony from the elements mentioned involves precipitation as Sb_2S_3 by hydrogen sulfide from sulfuric-tartaric acid medium in the presence of copper to act as a collector. This choice is somewhat arbitrary. Other methods which might have been investigated are extraction of antimony thionalate by organic solvents and extraction of antimony(III) iodide by benzene. Sulfide precipitation in sulfuric acid medium has already been shown to give satisfactory recovery of antimony from samples of bio material[5], in which, however, iron and other trouble-making elements are not present in notable amounts; a spectrographic method was used in the final determination. Attempts were made in the present work to isolate antimony by evolution as stibine by the action of zinc in mineral acid solution, but satisfactory recoveries could not be obtained.

Metals that must be separated with special care because of more or less sensitive color reactions with rhodamine B are iron(III), gallium, thallium(III), tungsten, and gold(III). Provision is made for the presence of these in the following procedure. The present method is not intended for samples containing much copper and other elements precipitated by hydrogen sulfide.

The final photometric determination is made essentially according to the directions of WEBSTER AND FAIRHALL[4].

Solutions

Hydroxylamine hydrochloride. (1) 10 g in 100 ml of water.
(2) 1 g in 100 ml of water.

Copper sulfate. 0.40 g of $CuSO_4 \cdot 5H_2O$ in 100 ml of water.

Sulfurous acid. Prepare fresh daily by saturating water with SO_2.

Isopropyl ether, peroxide-free. Treat as follows daily. In a separatory funnel shake 100 ml of ether with 10 ml of 2% $KMnO_4$ solution in $2N$ H_2SO_4 and drain off the latter. Repeat three times. Add 10 ml of sulfurous acid and shake. After draining off the aqueous phase, wash the ether phase three times with water, and finally with 50 ml of concentrated HCl.

Ceric ammonium sulfate, $0.1N$. 32 g of $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ in 500 ml of $1N$ H_2SO_4. Filter if necessary.

Rhodamine B. 0.20 g in 100 ml of water.

Standard antimony solution. Dissolve 0.0599 g of pure Sb_2O_3 in a small volume of concentrated HCl and dilute to 100 ml. The final HCl concentration should be $6N$. This solution contains 500 γ Sb per ml. Prepare a working standard by diluting 1.00 ml of this solution to 100 ml with $6N$ HCl (5.0 γ Sb per ml). The working standard should be prepared fresh weekly.

Procedure

To approximately 50 ml of solution, $0.5N$ in sulfuric (or hydrochloric) acid and containing 0.5-2.5 γ Sb, add 2 g of tartaric acid and 3 ml of hydroxylamine hydrochloride solution (1) (sufficient to reduce 0.1 g ferric iron). Heat to boiling and keep at the boiling point for 5-10 minutes. Cool and add 1.0 ml of copper sulfate solution. Pass a fairly rapid stream of hydrogen sulfide into the solution for 10 minutes, then heat to near boiling, and keep at this temperature for 5 minutes while continuing the passage of gas. During this time the precipitate should coagulate. Remove the beaker from the heat and bubble hydrogen sulfide through the solution for another 10 minutes. Set the solution aside for 3 hours, or preferably overnight.

Collect the precipitate in a small porcelain filter crucible and wash carefully three or four times with 2 ml portions of $0.5N$ sulfuric acid saturated with hydrogen sulfide. Discard the filtrate and washings. Add 3 ml of concentrated hydrochloric acid and 1 ml of concentrated nitric acid to the crucible to dissolve the precipitate. After a few minutes draw the acid through the crucible and wash with 5 ml of 1:1 nitric acid and finally with a little water. Evaporate the combined solutions in a small covered beaker on a steam bath or low temperature hot plate to a volume of a few drops. Add 0.5 ml of 1:2 sulfuric acid and heat just to fumes of sulfuric acid. Cool and add 5 ml of sulfurous acid solution. Cover the beaker and boil gently for 10 minutes or until the volume has been reduced to about 3.5 ml.

Cool and transfer the solution to a small short-stemmed separatory funnel and add 5 ml of concentrated hydrochloric acid to make the mixture 7*N* in hydrochloric acid. Cool to room temperature, add 5 ml of *iso*propyl ether and shake for 20-30 seconds. When the phases have separated run the aqueous layer into another separatory funnel (rinsed with 1:1 hydrochloric acid) and shake with another 5 ml portion of ether. Draw off the aqueous layer into a separatory funnel (rinsed with 1:1 hydrochloric acid) and wash the combined ether phases with 1 ml or less of 1:1 hydrochloric acid and add the latter to the aqueous phase.

To the aqueous solution add enough ceric ammonium sulfate solution to give a yellow color (about 2 ml is usually required), mix at once, and after exactly 1 minute blow air into the funnel for a few seconds to remove any free chlorine that may be present. Immediately add 5 drops of hydroxylamine hydrochloride solution (2), stopper the funnel and shake. The yellow color of ceric sulfate should disappear. Again blow air into the funnel for 15-20 seconds. Without delay add 3 ml of 85 per cent. phosphoric acid, mix, and follow with 1.0 ml of rhodamine B solution. Mix and add 5.0 ml of reagent-grade benzene. Shake vigorously for 1 minute to extract rhodamine B chloroantimonate. Allow the funnel to stand for about 5 minutes to allow droplets of water to separate from the benzene phase. Drain off and discard the aqueous layer. Dry the stem of the funnel with a roll of filter paper. Filter the benzene through a small plug of glass wool into a 1 cm cell. The solution should be entirely clear. Measure the transmittancy at 565 mμ.

Establish the standard curve by taking 0, 0.5, 1.0, 2.0 and 3.0 γ of antimony, adding 10 ml of 6*N* hydrochloric acid and 0.5 ml of ceric ammonium sulfate and proceeding as described above. Run a blank on the reagents.

For procedure in presence of thallium and gold see DISCUSSION.

Silicate rocks. Add 5 ml of 1:1 sulfuric acid and 10 ml of hydrofluoric acid to 1.0 g of 100-mesh rock powder in a platinum dish and evaporate to strong fumes of sulfuric acid. Cool, add 1 ml of 1:1 sulfuric acid and a few milliliters of water, and again evaporate to strong fumes. Cool, add a few milliliters of water, evaporate, and drive off the excess sulfuric acid. Treat the residue with 2 g of tartaric acid, 2.5 ml of 1:2 sulfuric acid and 25 ml of water. Heat to near the boiling point and keep at this temperature for 15-30 minutes with occasional stirring. Filter off the residue of calcium sulfate and any other insoluble material on a small paper of medium texture and wash with small portions of 0.1*N* sulfuric acid. Catch the filtrate in a beaker. The total volume should not exceed 50-60 ml. The insoluble material may be discarded. It will not contain appreciable amounts of antimony*. Then continue as in the general procedure above.

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* Except possibly when sulfides or carbonaceous material are present (shales). Then fuse with sodium peroxide in a nickel crucible, take up the melt in water, boil to decompose peroxide, add enough hydrochloric acid to make the acidity about 1*N*, heat to boiling, filter if necessary, and add the filtrate to the main solution.

DISCUSSION

Results obtained in applying the proposed method are collected in Tables I and II. A filter photometer with a 1 cm cell was used throughout (Leitz-Rouy, 550 mμ filter). The standard curve (log I_0/I *vs.* concentration) was linear up to 0.5 p.p.m. Sb in the benzene. The sensitivity was 0.004 γ Sb/cm^2 for log $I_0/I = 0.001$. Determinations listed in Table I were carried out on 50 ml of solution, 0.5N in sulfuric acid, with the additions shown. Phosphoric acid was not added in this series in the final photometric determination. It will be seen that the recovery of antimony is satisfactory with 1.5 mg of CuS (1 mg Cu) as collector. Ferric ion up to 500 mg does not interfere if it is reduced with hydroxylamine hydrochloride before the sulfide precipitation. If it is not reduced, the recovery

TABLE I

DETERMINATION OF ANTIMONY AFTER SULFIDE PRECIPITATION

Addition	Sb present,[a] γ	Sb found, γ
—	0.3	0.2, 0.2, 0.3
—	0.6	0.55, 0.6
—	1.1	1.0
—	2.1	2.0
— (HCl solution)	1.2	1.3, 1.1
— (HCl solution)	2.2	2.2, 2.3
60 mg Fe(III)	0.3	0.35, 0.3, 0.3
60 mg Fe(III)	0.6	0.6, 0.5
60 mg Fe(III)	1.1	0.9, 0.9, 1.3, 1.0[b]
60 mg Fe(III)	2.1	2.2, 1.9, 1.8,[b] 1.9[b]
60 mg Fe(III)	3.1	3.2, 3.3
100 mg Fe(III) (HCl solution)	1.2	1.0
500 mg Fe(III)[c]	1.2	1.0,[d] 1.3[e]
500 mg Fe(III)[c]	2.2	2.1,[d] 2.2[e]
100 mg Ni, 50 mg Co	1.1	1.2
1 ml H_3PO_4 (85%)	2.1	2.0
0.1 mg Ga[f]	0.3	0.35
0.1 mg Ga[f]	0.6	0.5, 0.5, 0.7
0.1 mg Ga[f]	1.1	1.3
1.0 mg W	1.1	1.1
0.1 mg Tl	0.1	0.8
0.1 mg Tl	1.1	1.8
0.1 mg Tl[g]	0.1	0.1, 0.1
0.1 mg Tl[g]	1.1	1.0, 1.2
0.1 mg Au[h]	1.1	0.9, 0.9

[a] Includes Sb in blank (0.1 γ with no addition and with 60 mg Fe(III), 1.2 γ with 500 mg Fe(III), and 1.1 γ with 1 ml H_3PO_4).

[b] 2 mg Cu^{+2} instead of 1 mg.

[c] 10 ml 10% $NH_2OH \cdot HCl$.

[d] Single sulfide precipitation, 3 ml of H_3PO_4 added in the determination.

[e] First sulfide precipitate dissolved in acid and reprecipitated with hydrogen sulfide.

[f] Double *iso*propyl ether extraction.

[g] Antimony separated from thallium by cupferron-chloroform extraction[1].

[h] Reduced gold filtered off (porous porcelain filter crucible).

of antimony is incomplete. Hydrochloric acid may be used in place of sulfuric acid for acidification. Increasing the acidity from 0.5 to 1.0*N* does not affect the recovery of antimony.

The color given by ferric ion with rhodamine B is about 0.01 as strong as the antimony color. From the results in Table I, it appears that with ∼ 60 mg Fe, the coprecipitation of iron is not serious. However, as a precautionary measure, phosphoric acid may be added to the final solution to prevent the reaction of any minute amounts of iron that may have contaminated the copper sulfide precipitate. As much as 0.2 mg Fe(III) is made harmless by 3 ml of 85 per cent. phosphoric acid*, and more iron than this is not to be expected in the sulfide precipitate.

Gallium is coprecipitated sufficiently with copper sulfide to require removal. The standard *iso*propyl ether extraction from ∼ 7*N* hydrochloric acid serves conveniently for the separation of gallium from antimony(III), since a high hydrochloric acid concentration is required in the subsequent antimony determination. As much as 100 γ of Ga can readily be removed in this way and doubtless more could be dealt with because the extraction coefficient (ether/aqueous phase) is about 200. The reaction of gallium with rhodamine B is so sensitive that 1 γ Ga will cause an error ($\equiv$ 0.3-0.4 γ Sb). Without ether extraction, 100 γ of gallium will lead to an error of +0.5 γ Sb under the conditions described (hydrogen sulfide precipitation). Thallium(III) gives a rather insensitive color reaction with rhodamine B but it is carried down with copper sulfide; less than 20 γ in the final solution causes no error in the antimony determination. As much as 40 γ of thallium in the original solution is permissible; amounts larger than this will rarely be encountered. If necessary, cupferron-chloroform extraction can be applied for separation of antimony from thallium[1]. Small amounts of gold do not interfere. Gold(III) is reduced to metal in the treatment with sulfur dioxide, and can be filtered off before the antimony-rhodamine B color is developed.

The effect of the following elements was tested directly by adding the amounts (mg) indicated to a solution subjected to rhodamine B extraction: Ag 0.1, Al 10, As(III) 0.1, B 0.1, Be 0.1, Bi 0.1, Cd 0.1, Co 1, Cr(III) 1, Cu 10, Ge 0.1, Hg(II) 1, In 0.1, Mo(VI) 0.1, Pb 1, Pd(II) 0.1, Pt(IV) 1, Sc 0.1, Se(IV) 0.1, Sn(II) 1, Ta 0.1, Te(IV) 0.1, Th 1, Ti 10, U 1, V(V) 0.1, W(VI) 0.1, Zn 1, Zr 1. None gave a color, and none interfered with the determination of 0.5 γ of Sb (0.4 to 0.6 γ found). Low results for antimony were obtained with 0.5 mg V. A precipitate was given by 1 mg W. In the presence of tartrate, vanadium and tungsten will not be precipitated by hydrogen sulfide.

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* We have found that reagent-grade 85 per cent. phosphoric acid treated with hydrogen sulfide according to the procedure above yields a color with rhodamine B equivalent to 1 γ Sb per milliliter of the acid. However, this antimony is present in inactive form in the phosphoric acid so that it gives no color when the acid is added in the final steps of the rhodamine B procedure.

A further test of the method was obtained by adding known amounts of antimony to 1.0 g of sample simulating a mafic rock (10 per cent. Fe) and decomposing with sulfuric-hydrofluoric acid. In this series phosphoric acid was added to the final solution before rhodamine B extraction. Recoveries are satisfactory, but tend to be low (Table II). The negative error does not seem to be due to incomplete precipitation of antimony, because addition of copper to the filtrate from the first sulfide precipitation and repetition of the precipitation does not result in the recovery of appreciable amounts of antimony. Possibly some loss of antimony takes place in the hydrofluoric acid decomposition. It should be pointed out that no significant loss of antimony occurs under the conditions specified when the hydrochloric-nitric acid solution of antimony sulfide is evaporated.

TABLE II

DETERMINATION OF ANTIMONY IN SYNTHETIC MAFIC ROCK[a]

Addition	Sb present,[b] p.p.m.	Sb found, p.p.m.
	0.15	0.0, 0.1, 0.3, 0.2
	0.65	0.5, 0.6, 0.6[c], 0.8
	1.15	0.9,[c] 0.9[d]
	2.15	1.7, 1.9
	3.15	2.8,[e] 2.8[e]
	5.15	4.8[f]
	7.15	6.8[g]
	10.15	9.3[h]
20 p.p.m. Tl	0.15	0.15
40 p.p.m. Tl	0.15	0.3
20 p.p.m. Tl	1.15	1.0
20 p.p.m. Tl, 3 p.p.m. I^-	0.15	0.2, 0.35
20 p.p.m. Tl, 3 p.p.m. I^-	1.15	1.4, 1.3
1000 p.p.m. V, 50 p.p.m. W	0.15	0.25
1000 p.p.m. V, 100 p.p.m. Sn, 100 p.p.m. W	0.15	0.35, 0.35
1000 p.p.m. V, 100 p.p.m. Sn, 50 p.p.m. W	1.15	1.3
1000 p.p.m. Nb, 500 p.p.m. Ta	0.15	0.3
1000 p.p.m. Nb, 500 p.p.m. Ta	1.15	1.05
100 p.p.m. Ga	1.15	0.9

[a] Percentage composition: 48 SiO_2, 12 Al_2O_3, 15 Fe_2O_3, 10 MgO, 10 CaO, 3(Na_2O + K_2O), 1.5 TiO_2, 0.3 P_2O_5, 0.25 MnO.

[b] Includes original Sb in sample, 0.15 p.p.m.

[c] To filtrate from sulfide precipitation 0.5 γ Sb and 1 mg Cu added and 0.5 γ Sb found after sulfide precipitation.

[d] To filtrate from sulfide precipitation 1.0 γ Sb and 1 mg Cu added and 1.0 γ Sb found.

[e] 10 ml of benzene used for extracting Sb-rhodamine B complex.

[f] 15 ml of benzene used for extracting Sb-rhodamine B complex.

[g] 20 ml of benzene used for extracting Sb-rhodamine B complex.

[h] 25 ml of benzene used for extracting Sb-rhodamine B complex.

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The lower limit of the rhodamine B method is determined more by the reproducibility than by the sensitivity. With 5 ml of benzene, variations of ± 0.1 γ Sb may occur. The sensitivity can be increased two or three-fold by using a spectrophotometer (565 mμ) in place of a filter photometer, but it is not certain that a net gain is obtained. Perhaps more intensive study of the rhodamine B-antimony color development will reveal conditions for somewhat better reproducibility. At present, with a 1 gram sample, the limit of the method, with separations, is 0.1-0.2 p.p.m. Sb.

SUMMARY

A method is described for the colorimetric determination of as little as a few tenths of a part per million of antimony in samples composed primarily of elements of atomic numbers 1-28 (*e.g.*, geo materials).

Antimony is isolated by sulfide precipitation in mineral acid medium after reduction of ferric iron with hydroxylamine hydrochloride, with final determination by rhodamine B-benzene extraction. The procedure provides for the presence of gallium, thallium, tungsten and gold.

RÉSUMÉ

Une méthode est décrite pour le dosage colorimétrique de faibles teneurs en antimoine (quelques dizièmes de partie par million), dans des échantillons composés principalement d'éléments de nombre atomique allant de 1 à 28.

L'antimoine est séparé par précipitation comme sulfure en solution acide, après réduction du fer(III) par le chlorhydrate d'hydroxylamine. Le dosage s'effectue par le procédé d'extraction rhodamine B-benzène. L'influence du gallium, du thallium, du tungstène et de l'or a été étudiée.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben für die kolorimetrische Bestimmung von schwachen Antimongehalten (einige Zehntel pro Million) in Proben, welche hauptsächlich aus Elementen bestehen mit Atomzahlen zwischen 1 und 28. Das Antimon wird abgetrennt durch Ausfällung als Sulfid in saurer Lösung, nachdem das Eisen(III) durch das Chlorhydrat von Hydroxylamin reduziert worden ist. Die Bestimmung erfolgt durch Extraktion mit Rhodamin-B-Benzol. Der Einfluss von Gallium, Thallium, Wolfram und Gold wurde untersucht.

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ETUDE DE L'APPLICATION DE L'*ISO*NITROSOMALONYLGUANIDINE AU DOSAGE DU FER DANS LES ALLIAGES D'ALUMINIUM ET DANS LES ZINCS ET AU DOSAGE DU COBALT DANS LES ACIERS

par

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1. Il est connu que le sel de nitroso-R, réactif classique du cobalt, s'applique également au dosage colorimétrique du fer.

On s'est proposé de savoir si l'*iso*nitrosomalonylguanidine[1], déjà appliqué au dosage du cobalt se prête également au dosage du fer.

2. On a profité de cette recherche pour examiner si la variante proposée par GALLEGO, DEIJS ET FELDMEIJER[2] pour le dosage du cobalt au moyen du nitroso-R était valable également pour le dosage au moyen de la nitrosomalonylguanidine.

PARTIE THEORIQUE

3. Le sel de sodium de l'acide nitroso-R donne, avec les sels ferreux, une coloration verte (VAN KLOOSTER[3]) et cette réaction est appliquée par SIDÉRIS[4] au microdosage du fer. La méthode est étudiée par GRIFFING ET MELLON[5]. Ces auteurs concluent à une sensibilité de ce réactif au moins égale à celles de la phénanthroline et du dipyridyle mais signalent l'interférence de différents éléments (Co, Cu, Ni, Ce, Cr, U). Cette limitation est palliée par DEAN ET LADY[6]; la méthode est également étudiée par OKA ET MIYAMOTO[7], et appliquée par MILNER ET NALL[8] et DEAN ET LADY[6] au dosage du fer dans les alliages légers, cuivreux etc . . .

4. Le pH doit être réglé vers pH 5 à 7; en présence de cuivre toutefois, qui précipite par réduction en milieu peu acide, et en présence d'aluminium celui-ci donnant la précipitation d'alumine ou de sels basiques, l'acidité doit être augmentée vers pH 3, et cela au détriment de la sensibilité de la mesure (DEAN ET LADY[6]); cet inconvénient est évité par introduction de cyanure (MILNER ET NALL[8]).

APPLICATION AU DOSAGE DU FER

5. L'étude de la méthode au sel de *nitroso-R* est faite selon la technique de DEAN ET LADY[6].

A la prise d'essai de sel ferrique (de la liqueur à 1 ml = 4 γ Fe, appendice 1, réactif[8], ajouter 0.5 ml de solution de chlorhydrate d'hydrazine (100 g/l), 10 ml de solution

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de sel de nitroso-R (10 g/l) et 20 ml de solution d'acétate d'ammonium 2*M* (154 g/l); chauffer à 95° et porter au bain-marie bouillant 5 à 10 min. Refroidir et compléter à 50 ml.

Le pH peut varier de 5 à 7, avec optimum à pH 6, conféré par l'acétate d'ammonium. Optimum de longueur d'onde pour la mesure photométrique: 700 mμ.

Des gammes faites avec des quantités de fer atteignant au maximum 60 γ se traduisent par une droite: densité optique = fonction du fer en oeuvre.

6. Selon un mode opératoire identique, la *nitrosomalonylguanidine* donne une coloration bleue, et la sensibilité est du même ordre que celle que confère le sel de nitroso-R. L'optimum de longueur d'onde se situe à 630 mμ (Fig. 1); l'optimum de pH se situe entre 5 à 6; l'intensité de la coloration décroit nettement au delà de pH 4 (Fig. 2).

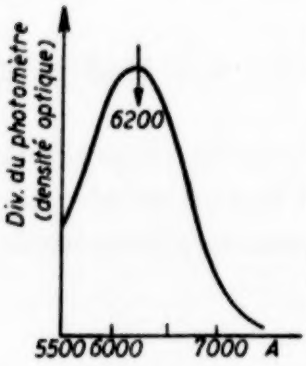

Fig. 1.

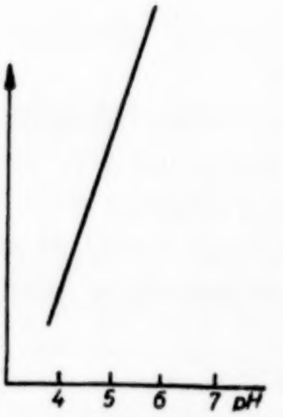

Fig. 2. Absorption en fonction du pH.

La courbe représentative du fer mesuré (jusqu'à 50 γ Fe), en fonction de la densité optique, est une droite.

7. Différents réactifs, déjà étudiés à propos du cobalt [1], ont été essayés par la même technique (§ 5) vis-à-vis du fer.

L'acide violurique et la 2.6-dioxy-4-amino 5-*iso*nitrosopyrimidine donnent vers pH 6 une coloration violette, dont le maximum d'absorption est 600 mμ; les variations de l'intensité de la coloration avec le pH sont analogues à celles que présente la nitrosomalonylguanidine, et ces réactifs se montrent moins sensibles que ce dernier.

L'acide *iso*nitrosothiobarbiturique donne une coloration verte vers pH 6, mais en l'absence de fer le milieu est coloré en brun.

L'*iso*nitroso-4-amino-6-oxy-2-thiopyrimidine ne réagit pas. L'*iso*nitrosoiminomalonylguanidine donne, à pH 6, une coloration verte, mais avec précipitation du réactif.

En définitive aucun de ces réactifs ne présente d'intérêt supérieur à la nitrosomalonylguanidine.

8. Ce dernier réactif a été étudié en vue d'application aux alliages d'aluminium et aux zincs.

A des doses de fer variables jusqu'à 100 γ Fe*, ajouter 1 ml de solution de chlorhydrate d'hydroxylamine (10 g/l), 10 ml de solution de nitrosomalonylguanidine (2 g/l), 50 ml de solution tampon d'acétate de sodium (50 g/l). On porte au bain-marie bouillant 5 à 10 min. Refroidir et compléter à 100 ml en fiole jaugée.

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* Les réactifs sont ceux indiqués en APPENDICE 1.

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La courbe de la densité optique en fonction de la concentration en fer est une droite ($\gamma = 630$ mμ).

Le *nickel* (10 ml d'une solution de chlorure de nickel crist. à 0.1 g/l Ni) ne modifie pas le résultat.

9. Le cuivre (10 ml d'une solution de sulfate de cuivre crist. à 0.35 g/l) laisse précipiter de l'oxydule de cuivre. L'addition au milieu de cyanure de potassium corrige ce phénomène, mais doit être limitée, sinon la coloration du fer se trouve diminuée: 2 ml de solution de cyanure de potassium à 10 g/l corrige l'influence du cuivre, sans atténuer la coloration du fer.

Des gammes à Fe variable, ainsi faites, donnent des résultats identiques à ceux obtenus précédemment, en l'absence de cuivre et de cyanure.

10. *L'aluminium* est introduit en essais selon le protocole suivant.

Attaque de 0.5 g d'aluminium pur par 10 ml d'acide chlorhydrique (1.18) *au demi* en présence de 1 ml de solution de chlorure de nickel (20 g/l). Compléter à 200 ml en fiole jaugée. De ce liquide, prélever 6 prises aliquotes de 10 ml que l'on reçoit dans 6 fioles jaugées de 100. Distribuer respectivement: 0-5-10-15-20-25 ml de liqueur ferrique (1 ml = 4 γ Fe), 1 ml de solution de chlorhydrate d'hydroxylamine (10 g/l), 2 ml de solution de cyanure de potassium (10 g/l), 5 ml de réactif (2 g/1) et 50 ml de tampon à l'acétate de sodium (50 g/l). Compléter à 100 ml, porter au bain-marie 5 à 10 min.

Il y a précipitation d'acétate basique d'aluminium hydrolysé.

Or, la réaction du fer a lieu à *froid*; il est donc nuisible de chauffer.

La gamme d'étalonnage obtenue à *froid* en présence d'aluminium, est identique à celle que l'on obtient à froid également en l'absence d'aluminium, les quantités de fer de l'une et l'autre gammes étant identiques. Il est donc inutile de préparer la gamme d'étalonnage avec des quantités d'aluminium égales à celles des essais: il est possible de ne pas mettre d'aluminium dans les termes de la gamme d'étalonnage.

Le *manganèse* n'a aucune influence sur ce dosage du fer.

11. *Dosage du fer dans les alliages; d'aluminium.* Le mode opératoire indiqué en APPENDICE 1 résulte de cette mise au point. Le Tableau I indique quelques résultats relevés à l'aide d'alliages à 4% Mg environ, et contenant en outre de petites quantités de cuivre, titane, manganèse, etc... La colonne 1 donne les résultats trouvés par la méthode à l'*iso*nitrosomalonylguanidine, la colonne 2 ceux de la méthode à l'acide sulfophénylpyrazolone carboxylique[9], laquelle a, vis-à-vis de la première, l'inconvénient de nécessiter la séparation du cuivre.

12. *Dosage du fer dans les zincs.* En milieu faiblement acide (pH 6.5 à 5), et en présence du zinc, la nitrosomalonylguanidine donne la coloration bleue avec les sels ferreux. La sensibilité augmente toutefois lorsque l'acidité diminue et tend vers pH 7, et il est préférable de se tenir vers pH 6 à 6.5, ce qu'assure le mode opératoire (APPENDICE 2 B).

La quantité absolue de zinc, présente dans la mesure colorimétrique, exerce une influence propre sur la coloration bleue du fer. Ainsi, avec 100 γ Fe, on relève les densités optiques, en présence de quantités variables de zinc, qu'indique le Tableau II.

Il est donc nécessaire que les gammes d'étalonnage comportent dans chacun des termes une quantité de zinc égale à celle qu'apporte l'essai.

TABLEAU I

Fe % Alliages d'Al	
1	2
0.228	0.21
0.216	0.21
0.264	0.26
0.23	0.23
0.23	0.24
0.295	0.31
0.306	0.30
0.286	0.28
0.336	0.33
0.23	0.22

TABLEAU II

Zn g	Densité optique
0.2	0.915
0.066	0.945
0.033	0.90
0	0.855

13. La sensibilité de la réaction, en milieu acide, ne permet pas d'atteindre aisément des taux inférieurs à 0.01 % Fe.

Or, la nitrosomalonylguanidine réagit avec les sels ferreux en milieu légèrement alcalin; la réaction faite en milieu tamponné acétique dans la plage alcaline donne lieu aux mesures que résume le Tableau III.

Comme en milieu acide, le zinc exerce une influence propre sur la coloration (Tableau IV), et par suite les teneurs des gammes d'étalonnage doivent également comporter une quantité de zinc égale à celle qu'apporte l'essai.

14. Les teneurs variables en fer à doser, prévues par la Norme de produits*, imposent un échelonnement correspondant des prises d'essai, ce que concrétise le mode opératoire (APPENDICE 2). Celui-ci a été appliqué à des zincs où le fer était dosé par la méthode à l'acide sulfosalicylique (Tableau V). Sur celle-ci, la méthode proposée présente des avantages de simplicité et de rapidité.

TABLEAU III

pH	Division de l'appareil
10.7	27
10.5	67
10.3	82
10	85.5
9.8	90
9.6	100

TABLEAU IV

Zn g	Division de l'appareil	pH
1	97	9.3
0.5	91	9.7
0.2	84.5	9.8
0.066	91	9.9
0.033	66.6	9.9
0	39	9.9

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* AFNor Pr A55—101.

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TABLEAU V

Qualité des zincs	Fe % a. sulfosal.	Fe % I.N.M.G.
Z 9	0.003.5	0.003.9
Z 9	0.004.1	0.004.7
Z 9	0.005.8	0.006.4
Z 8	0.003.7	0.004.05
Z 8	0.004.5	0.004.4
Z 8	0.006.5	0.006.3
Z 7	0.005	0.005.5
Z 6	0.01.9	0.01.6
Z 5	0.05.8	0.06.07
2 Z 6	0.07.7	0.07.72
2 Z 4	0.13	0.12.75

APPLICATION AU DOSAGE DU COBALT

15. Dans le dosage colorimétrique du cobalt, au moyen du *sel de nitroso-R*, GALLÉGO, DEIJS ET FELDMEIJER[2] décomposent l'excès de réactif et le complexe ferrique de celui-ci non par l'acide nitrique, mais par l'eau bromée et l'acide chlorhydrique: après formation du complexe cobaltique en milieu acéto-acétique, on ajoute 2 ml d'acide chlorhydrique (1.19) et 2 ml d'eau bromée saturée, repos de 8 à 10 min, une goutte de solution de sulfite de sodium (100 g/l) afin de réduire l'excès de brome.

L'on a appliqué cette modification au dosage du cobalt dans les aciers[10].

a) A des volumes variables d'une solution de sulfate de cobalt (1 ml = 0.02 mg Co), on ajoute: 10 ml de solution de sel de nitroso-R (5 g/l), 10 ml de solution d'acétate de sodium (500 g/l), bouillir, puis 5 ml d'acide nitrique (1.33). Ebullition 1 min. Refroidir, compléter à 100 ml en fiole jaugée. Résultats des mesures (en division du photomètre): col. 2 du Tableau VI (λ = 565 mμ).

b) Dans une série d'essais différents, après addition de l'acétate, ajouter 10 ml d'acide chlorhydrique (1.18), puis 2 ml d'eau bromée (10 ml de brome et 20 g de bromure de potassium par litre). Repos 10 min. Ebullition 1 min. Puis 1 ml de sotion de métabisulfite de sodium (100 g/l). Refroidir et compléter à 100 ml.

Résultats des mesures: col. 3 du Tableau VI.

Les deux procédés sont donc bien équivalents, comme l'indique la comparaison des colonnes 2 et 3.

L'acidité finale à peu d'influence sur la coloration, ce qui ressort de l'essai ci-après.

En présence de 0.5 mg de Co, on ajoute *in fine*, dans 5 essais, des volumes variables d'acide nitrique. La colonne 2 du Tableau VII indique les résultats des lectures photométriques (en divisions de l'appareil). Mêmes essais avec les mêmes volumes d'acide chlorhydrique que selon le mode opératoire modifié (b): résultats de la colonne 3 du Tableau VII.

16. *L'isonitrosomalonylguanidine* a été employée selon le mode opératoire afférent (1) avec des quantités de cobalt variables.

TABLEAU VI

Co	nitroso-R		n.m.guanid.	
mg	2	3	4	5
0.5	100	100	100	100
0.4	81	80	81	81
0.3	61	60	60.5	61
0.2	41	40	40	41
0.1	21	21	20	20.5
0	0	0	0	0

TABLEAU VII

Acide ajouté ml	nitroso-R		n.m.guanid.	
	2	3	4	5
5	66.5	62		
8	65.5	62	90	87.5
10	65.5	60	90	89.5
12			92.5	89.5
15	65	60	97.5	96
20	65	56	106	101

Après addition du phosphate d'ammonium, on ajoute:

a) soit l'acide nitrique,

b) soit 10 ml d'acide chlorhydrique (1.18) et 2 ml d'eau bromée; repos 5 min; puis 1 ml de la solution de métabisulfite de sodium, et compléter à 100 ml.

Les résultats sont notés col. 4 et 5 du Tableau VI (en divisions de l'appareil).

Les essais à acidité finale variable sont indiqués dans les colonnes 4 et 5 du Tableau VII.

En présence de 0.5 mg Co, on ajoute, après le phosphate d'ammonium:

a) soit l'acide nitrique en quantités variables,

b) soit l'acide chlorhydrique en quantités variables, suivi des additions de l'eau bromée et du métabisulfite.

L'acidité du milieu réalisé in fine ayant donc une action sur l'intensité de la coloration lue, ainsi qu'il résulte de la comparaison des chiffres des colonnes 4 et 5 du Tableau VII, il est nécessaire de la réaliser égale, et dans les termes de la gamme, et dans les essais de dosage du cobalt.

Le procédé à l'acide nitrique, et celui à l'acide chlorhydrique bromé, sont l'un et l'autre équivalents à ce point de vue. Il apparait de plus que la méthode à l'*iso*nitrosomalonylguanidine étant plus sensible à l'acidité finale que celle qui fait usage du sel de nitroso-R, le complexe cobaltique du premier réactif se montre moins stable, plus dissocié, que le complexe cobaltique correspondant du sel de nitroso-R.

L'ensemble des résultats précédents subsiste quant aux conclusions lorsque du fer est en présence.

CONCLUSIONS

17. L'*iso*nitrosomalonylguanidine donne, avec les sels ferreux, en milieu acide (pH 6 environ) ou alcalin (pH 9 environ) une coloration bleue. Cette observation con-

stitue le principe d'une méthode de dosage du fer dans les alliages d'aluminium (en milieu acide) et d'une méthode de dosage du fer dans les zincs (deux cas sont prévus, l'un en milieu acide pour les plus fortes teneurs, l'autre en milieu alcalin pour les plus faibles teneurs, la coloration étant dans ce cas plus sensible).

Ces méthodes présentent des avantages sur les méthodes classiques employant respectivement l'acide sulfophénylpyrazolone carboxylique et l'acide sulfosalicylique.

18. Dans la méthode de dosage du cobalt par ce même réactif, on peut recourir à la modification de détail du mode opératoire que représente la substitution du brome à l'acide nitrique pour détruire l'excès de réactif.

APPENDICE I

Dosage du fer dans les alliages légers

Principe

La nitrosomalonylguanidine donne, avec les sels ferreux, vers pH 6, une coloration bleue. Le fer est maintenu à l'état ferreux par le chlorhydrate d'hydroxylamine. La densité optique est déterminée au photomètre (λ = 630 mμ).

Réactifs

1 — Acide chlorhydrique d = 1.18 *au demi.*
1′— Dilution d'acide chlorhydrique d = 1.18 à 10 ml pour un litre.
2 — Solution de chlorure de nickel crist. à 20 g/l.
3 — Eau oxygénée 100 vol.
4 — Solution de chlorhydrate d'hydroxylamine 10 g/l.
5 — Solution de cyanure de potassium 10 g/l.
6 — Réactif: solution de nitrosomalonylguanidine à 2 g/l.
7 — Tampon: solution d'acétate de sodium à 50 g/l.
8 — Liqueur ferrique. Attaquer 0.40 g de fer pur par 20 ml d'acide chlorhydrique au 1/2 (1). Diluer à 1 litre (1 ml = 0.000.4 g Fe). Prélever 10 ml de ce liquide. Ajouter 10 ml d'acide chlorhydrique (1.18) et diluer au litre (1 ml = 0.000.004 g Fe).

Mode opératoire

Prise d'essai: 0.5 g
1) Attaque par 10 ml d'acide chlorhydrique au 1/2 (1) en présence de 1 ml de solution de chlorure de nickel (2). Oxyder par une goutte d'eau oxygénée 100 vol (3). Porter à l'ébullition 3 min environ. Reprendre par de l'eau et compléter, en fiole jaugée de 200 ml à ce volume.
2) Prélever 10 ml de ce liquide, les recevoir en fiole jaugée de 100 ml.

3) Ajouter successivement en agitant

1 ml de solution de chlorhydrate d'hydroxylamine (4). Repos quelques minutes.

2 ml de solution de cyanure de potassium (5) (Si une précipitation d'alumine hydratée se produit, ajouter une goutte d'acide chlorhydrique au demi (1)).

5 ml de réactif (6)

50 ml de tampon (7)

et de l'eau pour compléter à 100 ml.

4) Mesurer parallèlement un essai à blanc avec les réactifs (sans prise d'essai de métal).

5) *Gamme d'étalonnage*

Dans 6 fioles jaugées de 100 ml, distribuer: liqueur type de fer (8) (1 ml = 4 γ Fe):
0—5—10—15—20—25 ml
et acide chlorhydrique (à 10 ml par litre) (1'):
25—20—15—10—5—0 ml
Opérer selon opér. 3.

6) *Mesures photométriques* ($\lambda = 630$ mμ)

Mesurer les 5 termes de la gamme par rapport à l'essai 0 Fe de la gamme.
Mesurer les essais par rapport à l'essai à blanc (op.4)*.

7) *Expression des résultats*

Les termes de la gamme contiennent respectivement:
20—40—60—80—100 γ Fe
soit 0.08—0.16—0.24—0.32—0.4% Fe du métal

Lire sur la droite d'étalonnage (densité optique = fonction du fer mesuré) le taux cherché: Fe %.

APPENDICE 2

Dosage du fer dans les zincs

Principe

La nitrosomalonylguanidine donne, avec les sels ferreux, une coloration bleue à pH 6 environ, et également à pH 9 pour lequel la réaction est plus sensible. Le fer est maintenu à l'état ferreux par le chlorhydrate d'hydroxylamine. La densité optique est déterminée au photomètre.

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* Cuves de 3 cm avec le photomètre M. JEAN ET R. CONSTANT.

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Réactifs

1 — Acide chlorhydrique (d = 1.18) *au demi*
2 — Acide acétique cristallisable
3 — Eau oxygénée (100 vol)
4 — Lessive de soude à 400 g/l
5 — Ammoniaque d = 0.9
6 — Solution de chlorhydrate d'hydroxylamine 10 g/l
7 — Solution de cyanure de potassium 10 g/l
8 — Réactif: solution d'*iso*nitrosomalonylguanidine à 2 g/l
9 — Tampon: solution d'acétate de sodium à 250 g/l
10 — Liqueur ferrique. Attaquer 0.40 g de fer pur par 20 ml d'acide chlorhydrique au 1/2 (1). Diluer à 1 litre (1 ml = 0.000,4 g Fe)
11 — Prélever 10 ml de ce liquide, ajouter 10 ml d'acide chlorhydrique (1.18) et diluer au litre (1 ml = 0.000,004 g Fe)
12 — Prélever 5 ml de la liqueur (10), ajouter 10 ml d'acide chlorhydrique (1.18) et diluer au litre (1 ml = 0.000,002 g Fe)
13 — Indicateur bleu de thymol — 0.1 g de matière colorante en poudre est mis en solution dans 15 ml d'eau environ, ajouter 4.3 ml de liqueur de soude *N*/20, chauffer légèrement pour dissoudre. Etendre d'eau à 500 ml en fiole jaugée.

A. *Modes opératoires en milieu alcalin*

1er cas: Zn compris entre 0.001 et 0.005 % (Zincs Z 9)
et 2ème cas: Zn compris entre 0.005 et 0.01 % (Zincs Z 8)

Prises d'essai

1er cas: p.e. = 1 g
2ème cas: p.e. = 0.5 g

1) Attaque par 10 ml d'acide chlorhydrique (1) au 1/2. Oxyder par 1 goutte d'eau oxygénée (100 vol) (3). Evaporer à 2 ou 3 ml, reprendre par 20 ml d'eau. Transvaser en fiole jaugée (100).

2) Ajouter deux gouttes d'indicateur au bleu de thymol (13), puis goutte à goutte de la soude (400 g/l) (4) jusqu'à virage au jaune, enfin de l'acide chlorhydrique (1) au *demi* jusqu'à virage au rose.

Ajouter successivement et en agitant après chaque addition:
1 ml de solution de chlorhydrate d'hydroxylamine (10 g/l) (6), 2 ml de solution de cyanure de potassium (10 g/l) (7), 5 ml de réactif (2 g/l) (8), 5 ml d'acide acétique (2), 15 ml d'ammoniaque (5), enfin 15 ml de solution d'acétate de sodium (250 g/l) (9). Compléter à 100 ml avec de l'eau.

3) Mener parallèlement un essai à blanc avec les réactifs (sans prise d'essai de métal)

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4) *Gamme d'étalonnage*

Attaquer 10 g de zinc, de qualité la plus pure possible (zinc Z 9 très peu riche en fer) par 100 ml d'acide chlorhydrique au 1/2 (1). Oxyder par 1 goutte d'eau oxygénée 100 vol (3). Evaporer jusqu'à 20 ml environ. Reprendre par de l'eau. Compléter à 100 ml en fiole jaugée. Ceci vaut pour *le premier cas*. Pour le *second cas*, diluer *au demi* cette solution, avec de l'eau.
Premier cas. Prélever 6 parties aliquotes de 10 ml chacune de la liqueur de zinc correspondante (10 g de zinc dans 100 ml), que l'on distribue respectivement dans 6 fioles jaugées (100). Distribuer respectivement: 0—5—10—15—20—25 ml de liqueur ferrique (1 ml = 2 γ Fe)[12].
Poursuivre selon le mode opératoire, op. 2 (ajouter deux gouttes de bleu de thymol etc . . .).
Deuxième cas. Opérer de même, à l'aide de la liqueur de zinc *diluée au demi*.

5) *Mesures photométriques* (λ=630 mμ)

Mesurer les 5 termes de la gamme par rapport à l'essai 0 Fe de la gamme. Mesurer les essais par rapport à l'essai à blanc (op. 3)*.

6) *Expression des résultats*

Les termes des gammes contiennent respectivement:
10—20—30—40—50 γ Fe
soit 1er cas: 0.001—0.002—0.003—0.004—0.005 % Fe
et 2ème cas: 0.002—0.004—0.006—0.008—0.01 % Fe
Lire sur la droite d'étalonnage (densité optique = fonction du fer mesuré) le taux cherché: Fe %.

B. *Modes opératoires en milieu acide*

3ème cas: Zn compris entre 0.01 et 0.05% (zincs Z 7 et Z6)
4ème cas: Zn compris entre 0.03 et 0.15% (zincs Z 5, 2 Z 6, 2 Z 5 et 2 Z 4)
5ème cas: Zn compris entre 0.06 et 0.3 % (zincs 2 Z 4)

Prises d'essai

3ème cas: p.e. = 1 g
4ème cas: p.e. = 1 g
5ème cas: p.e. = 0.5 g

1) *Attaque.* 3ème et 4ème cas par 10 ml d'acide chlorhydrique au 1/2 (1)
5ème cas par 5 ml d'acide chlorhydrique au 1/2 (1)
Oxyder par 1 goutte d'eau oxygénée (100 vol) (3). Evaporer (3ème et 4ème cas seulement) à 5 ml environ. Reprendre par 20 ml d'eau environ. Transvaser en fioles jaugées de:

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* Cuves de 4 cm avec le photomètre M. JEAN ET R. CONSTANT.

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3ème cas: 50 ml — 4ème et 5ème cas = 150 ml
Prélever, quel que soit le cas, une prise d'essai de 10 ml que l'on reçoit en fiole jaugée (100).

2) Ajouter deux gouttes d'indicateur au bleu de thymol (13), puis goutte à goutte de la soude (400 g/l) (4) jusqu'à virage au jaune, enfin de l'acide chlorhydrique (1) *au demi* jusqu'à virage au rose.

Ajouter successivement et en agitant après chaque addition:

1 ml de solution de chlorhydrate d'hydroxylamine (10 g/l) (6),
2 ml de solution de cyanure de potassium (10 g/l) (7),
5 ml de réactif (2 g/l) (8),
enfin 50 ml de solution d'acétate de sodium (250 g/l) (9). Compléter à 100 ml avec de l'eau.

3) Mener parallèlement un essai à blanc avec les réactifs (sans prise d'essai de métal).

4) *Gammes d'étalonnage*

Peser les prises d'essai suivantes de zinc, de qualité la plus pure possible (zinc Z 9).
3ème cas: p.e. = 2 g. Attaque: 20 ml d'acide chlorhydrique au 1/2 (1)
4ème cas: p.e. = 1 g. Attaque: 10 ml d'acide chlorhydrique au 1/2 (1)
5ème cas: p.e. = 0.5 g. Attaque: 5 ml d'acide chlorhydrique au 1/2 (1)

Attaque par les quantités indiquées ci-dessus d'acide chlorhydrique au 1/2 (1). Oxyder par 1 goutte d'eau oxygénée (100 vol) (3). Evaporer (3ème et 4ème cas seulement) à 5 ml environ. Transvaser en fioles jaugées de:

3ème cas: 100 ml; 4ème et 5ème cas; 150 ml.
Prélever, quelque soit le cas, 6 parties aliquotes de 10 ml (des unes ou des autres fioles jaugées, selon le cas), que l'on distribue dans 6 fioles jaugées (100). Distribuer respectivement: 0—5—10—15—20—25 ml de liqueur ferrique (1 ml = 4 γ Fe) (III). Poursuivre le mode opératoire B (oper. 2).

5) *Mesures photométriques* (λ=630 mμ)

Mesurer les 5 termes de la gamme par rapport à l'essai 0 Fe de la gamme. Mesurer les essais par rapport à l'essai à blanc (oper. 3)*.

6) *Expression des résultats*

Les termes des gammes contiennent respectivement:
20—40—60—80—100 γ Fe

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* Cuves de 3 cm avec photomètre M. JEAN ET R. CONSTANT.

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soit 3ème cas:

0.01—0.02—0.03—0.04—0.05 % Fe

4ème cas:

0.03—0.06—0.09—0.12—0.15 % Fe

5ème cas:

0.06—0.12—0.18—0.24—0.30 % Fe

Lire sur la droite d'étalonnage (densité optique = fonction du fer mesure) le taux cherché: Fe %.

SUMMARY

*Iso*nitrosomalonylguanidine reacts with iron salts in acid medium (pH *ca.* 6); or in basic medium (pH *ca.* 9), giving a blue color. This reaction is the basis of a new method for the determination of iron in aluminium alloys (in acid medium) or in zincs (in acid medium or in basic medium) for the weakest contents. Concerning the determination of cobalt in steels, bromine can be used instead of nitric acid, in order to remove the excess of reagent.

RÉSUMÉ

L'*iso*nitrosomalonylguanidine réagit avec les sels ferreux, en milieu acide (pH 6 environ) ou alcalin (pH 9 environ), en donnant une coloration bleue. Cette réaction constitue le principe d'une nouvelle méthode de dosage du fer dans les alliages d'aluminium (en milieu acide), et dans les zincs (en milieu acide, ou pour les teneurs en fer les plus faibles en milieu alcalin).

Concernant le dosage du cobalt dans les aciers, il est possible de remplacer l'acide nitrique, par le brome, pour détruire l'excès de réactif.

ZUSAMMENFASSUNG

*Iso*nitrosomalonylguanidin reagiert mit Eisensalzen in saurer Lösung (pH ungefähr 6) oder in alkalischer Lösung (pH ungefähr 9) und ergibt eine Blaufärbung. Diese Reaktion stellt ein neues Verfahren der Dosierung von Eisen in Aluminium-Legierungen (in saurer Lösung) und in Zinklegierungen (in saurer Lösung, oder für schwächste Eisengehalte in alkalischer Lösung) dar.

Bei der Bestimmung von Kobalt in Stählen ist es möglich, die Salpetersäure durch Brom zu ersetzen, um den Überschuss an Reagenz zu vernichten.

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SPECTROPHOTOMETRIC STUDY OF THE COMPOUNDS OBTAINED WITH SCHIFF'S REAGENT AND ACETALDEHYDE

by

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The use of Schiff's reagent for both the qualitative and quantitative estimations of aldehydes has been known for a long time[1,2]. WIELAND[3] suggested a probable formula for the Schiff's reagent and also the mechanism of its reaction with aldehydes. He pointed out that one or two molecules of SO_2 are taken up per molecule of fuchsin and form sulphanilic groups when fuchsin is rendered colourless. Aldehydes form with the reagent additive or loose complex compounds which rearrange themselves to differently coloured substances with the concomitant elimination of an H_2SO_3 molecule. He further suggested that after some time, aldehydes are detached from the complex to form aldehyde bisulphite, with H_2SO_3 remaining in excess; in consequence the decolourization of the liquid occurs.

HOFFPAUIR[4] showed that the intensity of the coloured compound obtained by the addition of formaldehyde to Schiff's reagent falls off somewhat rapidly after attaining a maximum. The work of HOFFPAUIR has not, however, been followed up systematically with the object of ascertaining the nature of the colored complexes. The present study is an attempt in this direction. Experimental results with acetaldehyde and the reagent indicate, under suitable conditions, the presence of five different compounds having characteristic absorption maxima.

EXPERIMENTAL

A B.D.H. sample of fuchsin was crystallized before use. Merck's acetaldehyde was used without further purification.

Schiff's reagent was prepared according to TOBIE's[5] method. 0.5 g of fuchsin was decolourised by the calculated amount of H_2SO_3 so as to maintain 2 g of SO_2 per litre, and the volume was made up to 1000 ml. The solution after being stored overnight showed a light yellow colour which was removed by treatment with the minimum amount of activated charcoal.

Spectrophotometric measurements were made with a Beckman's spectrophotometer (Model DU) with a slit width of 0.04 mm. The fuchsin solution was analysed throughout the entire visible wavelength range and was found to produce its characteristic peak at 535 mμ (A). A small amount of acetaldehyde with Schiff's reagent produces peak at 545 mμ (B), and after keeping overnight, fuchsin itself (A) is regenerated. In presence of a large excess of acetaldehyde not only does the peak shift to longer wavelength 555 mμ (C), but new maxima arise with time. For instance, after 3 hours the same solution showed another peak at 575 mμ (D), while after about a weak this solution gave rise to two more new peaks one at a shorter wavelength, 525 mμ (E), and another at 615 mμ (F). The peak "E" is not very well marked.

The above solution, after being stored for about a week, was saturated with NaCl and filtered. The filtrate was coloured green, having an absorption peak at 615 mμ (F); the residue was treated with a small amount of water and again filtered. The filtrate was coloured blue; corresponding to the peak at 575 mμ (D).

For identification of such compounds the following procedure was adopted.

Fuchsin solution, instead of the Schiff's reagent, was allowed to react with excess of acetaldehyde and kept for a few days. The solution on analysis showed only one peak at 525 mμ (E). This solution was treated with syrupy phosphoric acid or acetic anhydride and refluxed for some time. The solution on analysis showed peaks at 575 mμ (D) and at 615 mμ (F). The two compounds D and F were separated by salting out as previously mentioned. The separated compounds showed their characteristic peaks. The results of the experiments are presented in the graphs.

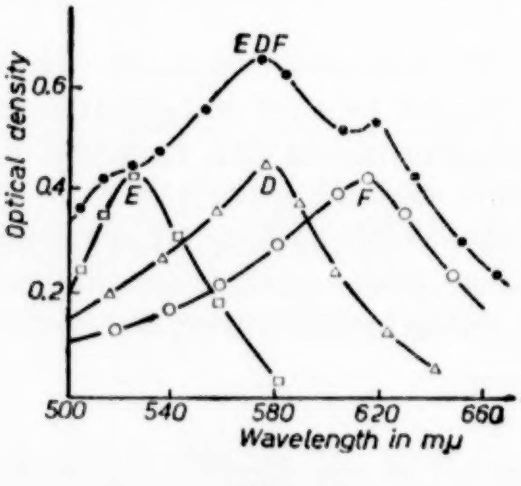

Fig. 1

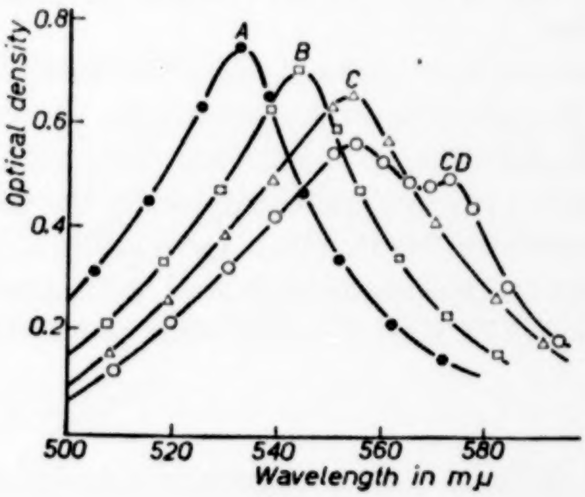

Fig. 2

DISCUSSION

The compound B is probably obtained when only one molecule of acetaldehyde adds on to the molecule of the reagent. This may be realized in the presence of a comparatively small amount of acetaldehyde. "B" is not very stable since, on standing overnight, fuchsin itself is regenerated. But in the presence of excess acetaldehyde, two molecules of it combine with the reagent to form the complex C.

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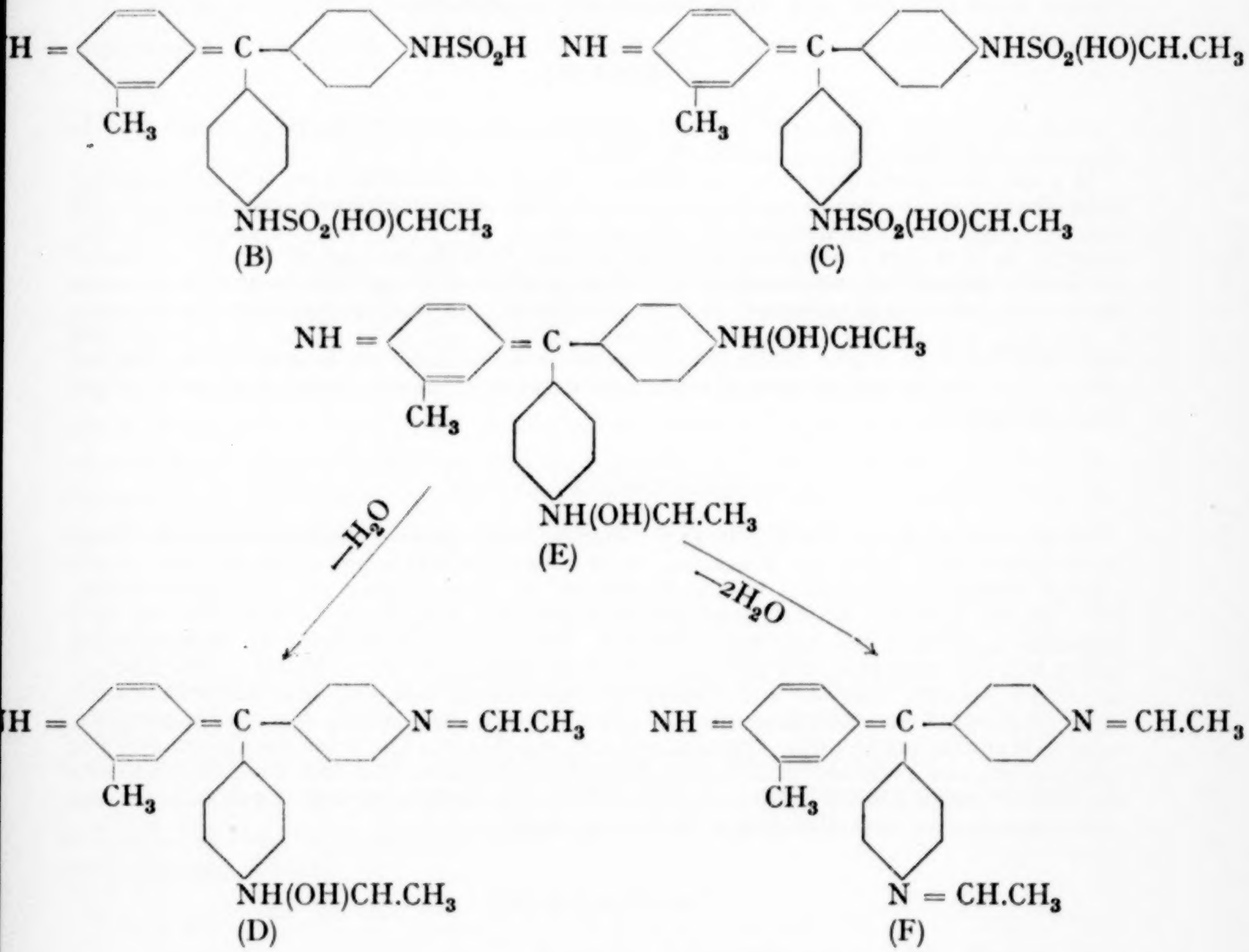
The compound E, which is formed only in the presence of a large excess of acetaldehyde and on keeping, may be considered to be composed of two molecules of acetaldehyde to one of fuchsin itself. As shown above, D is also formed by treating E with a dehydrating agent like syrupy phosphoric acid or acetic anhydride; it is likely, therefore, that D is derived from E by the elimination of a molecule of water. Further dehydration *i.e.* loss of another molecule of water from E possibly gives F.

These steps may be represented as follows:


H =
= C
NHSO$_2$H
CH$_3$
NHSO$_2$(HO)CHCH$_3$
(B)
NH =
= C
NHSO$_2$(HO)CH.CH$_3$
CH$_3$
NHSO$_2$(HO)CH.CH$_3$
(C)
NH =
= C
NH(OH)CHCH$_3$
CH$_3$
NH(OH)CH.CH$_3$
(E)
—H$_2$O
—2H$_2$O
H =
= C
N = CH.CH$_3$
CH$_3$
NH(OH)CH.CH$_3$
(D)
NH =
= C
N = CH.CH$_3$
CH$_3$
N = CH.CH$_3$
(F)

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SUMMARY

Five different compounds have been identified spectrophotometrically in the reaction between acetaldehyde and Schiff's reagent.

It has been found that, with a small amount of acetaldehyde, a complex with only one molecule of acetaldehyde for every molecule of the reagent is formed. This shows the peak at 545 mμ.

With excess of acetaldehyde, the complex contains two molecules of aldehyde per molecule of Schiff's reagent, corresponding to the peak at 555 mμ. After standing for some time, the solution containing this compound, gradually shows the presence of three new compounds, having peaks at 525 mμ, 575 mμ and 615 mμ. The former results from the interaction of two molecules of acetaldehyde and a molecule of fuchsin derived from Schiff's reagent itself. The other two are formed when the former loses one and two water molecules, respectively.

RÉSUMÉ

Cinq composés différents ont été identifiés spectrophotométriquement par la réaction acétaldéhyde — réactif de Schiff.

Il a été démontré que pour de faibles teneurs en acétaldéhyde, il y a formation d'un complexe ne renfermant qu'une molécule d'acétaldéhyde par molécule de réactif, présentant un maximum d'absorption à 545 mμ. Pour un excès d'acétaldéhyde, le complexe renferme deux molécules d'aldéhyde par molécule de réactif de Schiff, présentant un maximum d'absorption à 555 mμ. Au bout d'un certain temps, on constate la présence de trois nouveaux composés présentant des maxima à 525 mμ, 575 mμ et 615 mμ; le premier résulte de l'interaction de 2 molécules d'acétaldéhyde et d'une molécule de fuchsine provenant du réactif de Schiff luimême. Les deux autres sont formés par départ d'une ou deux molécules d'eau respectivement.

ZUSAMMENFASSUNG

Fünf verschiedene Verbindungen wurden auf spektrophotometrischem Wege identifiziert mit Hilfe der Reaktion Acetaldehyd-Schiff'sches Reaktiv. Es wurde gezeigt, dass sich bei kleinen Konzentrationen an Acetaldehyd ein Komplex bildet, der nur ein Molekül Acetaldehyd pro Molekül des Reaktives besitzt und ein Absorptionsmaximum bei 545 mμ aufweist. Bei einem Überschuss an Acetaldehyd bildet sich ein Komplex, welcher zwei Moleküle Acetaldehyd pro Molekül Schiff'schen Reaktivs besitzt, welcher ein Absorptionsmaximum bei 555 mμ aufweist. Nach einer gewissen Zeit stellt man die Anwesenheit von drei neuen Verbindungen fest, welche Maxima bei 525 mμ, 575 mμ und 615 mμ zeigen. Die erste resultiert von der Interaktion von zwei Molekülen Acetaldehyd und einem Molekül Fuchsin, welches vom Schiff'schen Reaktiv selber herrührt. Die zwei andern werden durch Abspaltung von einem bezw. zwei Molekülen Wasser gebildet.

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THE MECHANISM OF THE PLATINUM INDICATOR ELECTRODE IN ARGENTOMETRY

by

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INTRODUCTION

In the potentiometric titration of halides with silver nitrate, a silver indicator electrode is normally used and the theory underlying the process is quite straightforward. It was shown by MÜLLER[1], however, that platinum, gold, and a number of other inert electrodes also underwent a change of potential at the end-point in such titrations, and a platinum electrode has been used in argentometry[2] and in a very precise method[3] for the determination of the salinity of sea water where it appears to be superior to the silver electrode. It is by no means obvious why an inert electrode such as platinum should respond to changes in the concentration of silver ions, and the object of the present work was to ascertain the nature and mechanism of the potential which is set up.

EXPERIMENTAL

Potentiometric titration curves were obtained at room temperature (18° C) in the conventional way using a potentiometer-voltmeter circuit. The indicator electrodes were, in general, thick wires sealed into glass tubes so as to expose an area of 1 sq.cm; the reference electrode was a mercury-mercurous sulphate half cell (Hg/Hg_2SO_4 in saturated K_2SO_4). All potentials quoted are expressed on the hydrogen scale.

RESULTS

Effect of pre-treatment of platinum surface. In Fig. 1 are shown four curves for the titration of 25 ml of 0.1N sodium chloride with 0.1N silver nitrate using a platinum indicator electrode which had been treated in various ways. Curve 1 was obtained with a platinum electrode which had been immersed in cold concentrated hydrochloric acid for 1 hour and rinsed with distilled water before use. Curve 2 was that observed with a platinum electrode which, after cleaning in cold concentrated hydrochloric acid, was heated to redness for 5 min and then used in the titration. Curve 3 was found with a platinum electrode which had either been immersed in 50% ammonia solution for 30 min before use, or had been anodically polarized in 1*N* sulphuric acid (100 milliamp for 15 min). Curve 4 was obtained with a platinum electrode which had been cathodically polarized (100 milliamp for 15 min) in either 1*N* sulphuric acid or 1*N* sodium hydroxide, and this curve was identical with that using a silver indicator electrode. The above curves were found to be quite reproducible, although other methods of treatment of the platinum such as cleaning in warm concentrated nitric acid, or by anodic polarization in 1*N* sodium hydroxide gave rather erratic results.

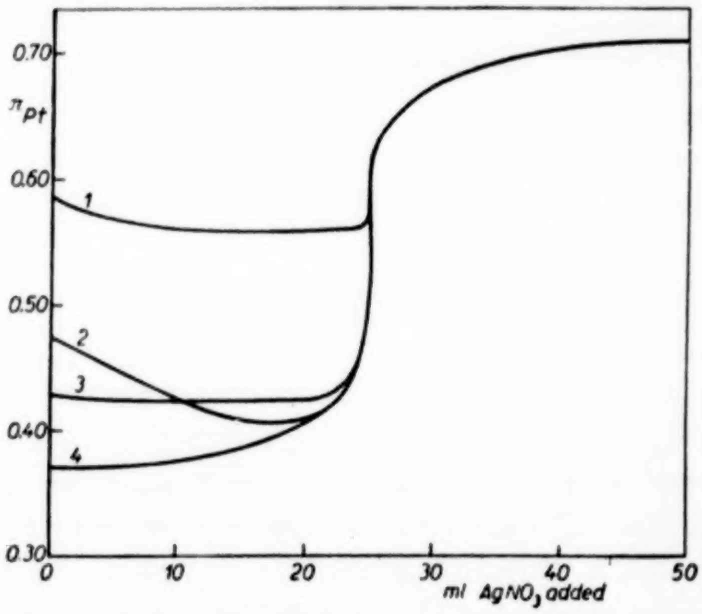

Fig. 1. Potentiometric titration of chloride with platinum indicator electrode.

It is noteworthy that at the end-point of the titration and when the silver nitrate is present in excess, all the curves in Fig. 1 merge and coincide with that found using a silver electrode. It is in the early stages of the titration that the potentials differ, and methods of treatment tending to reduce the platinum surface give the nearest approach to the behaviour of a silver electrode.

Establishment of equilibrium between platinum and silver ions. On immersion of a platinum electrode (cleaned by cathodic polarization) in solutions of silver nitrate of different concentrations, the potential ultimately reached was practically identical with that found for a silver electrode in the same solution. An appreciable time, however, was required for the potential to become steady, the time being longer the lower the concentration of silver ions. This is illustrated by the potential/time graphs in Fig. 2. No steady reproducible potential was reached on immersion of a clean platinum electrode in sodium chloride solutions, showing that its potential is not directly responsive to halide ions.

Detection of silver on the platinum surface. The previous experiments strongly suggest that a clean platinum electrode becomes coated with silver on dipping into a solution of silver ions. That this is so has been demonstrated analytically. The property of silver ions in catalysing the oxidation of manganous sulphate to permanganate by ammonium persulphate has been used to provide a very sensitive test for silver. It was found experimentally that on boiling 2 drops of 0.01M $MnSO_4$ with 10 ml of 0.1M $(NH_4)_2S_2O_8$ + 2N HNO_3 a red colour would develop in the presence of silver ions at a concentration of approximately 10^{-6} g ion/litre. A sheet of platinum foil of 100 sq.cm area was wrapped in a loose spiral, and after cleaning was cathodically polarized in 1N sodium hydroxide solution; it was then washed and immersed in 1N silver nitrate for 10 min. The platinum was then withdrawn and washed repeatedly with distilled water until the washings gave no reaction for silver by the above test. When the platinum had been washed completely free from silver ions, it was immersed in the reagent mixture so that the nitric acid present could dissolve any metallic silver on the surface. The test solution was then boiled and an unmistakable pink coloration developed. Repetition of the experiment with the platinum treated in different ways showed that only such pretreatment as led to a reduction of the surface and a lowering of its potential would lead to a positive reaction for silver; anodic treatment of the platinum or cleaning it with hot concentrated nitric acid gave negative results.

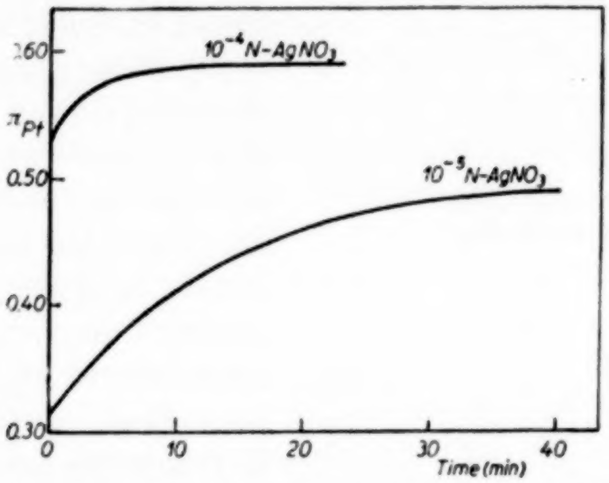

Fig. 2. Potential of platinum in solutions of silver ions.

To obtain some quantitative idea of the amount of silver present, an electrometric method was used. A platinum electrode of 1 sq.cm area was cathodically treated in sodium hydroxide and was then anodically polarized in 0.1M potassium nitrate as electrolyte at a constant current of 10 microamp, its potential relative to the reference electrode being measured on a valve-voltmeter at various times so

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that a charging curve could be constructed. The experiment was then repeated with the electrode after it had been immersed in 1N silver nitrate solution for 10 min. The charging curves are shown in Fig. 3, and it is at once apparent that after immersion in silver nitrate the electrode shows a well-defined arrest corresponding to the ionization of silver. The quantity of electricity passed in the arrest is approximately 3500 microcoulombs corresponding to *ca.* $3.6 \cdot 10^{-8}$ g atom of silver, or about $2.2 \cdot 10^{16}$ atoms of Ag. Taking the diameter of the silver atom to be $2.6 \cdot 10^{-8}$ cm, there would be about $1.5 \cdot 10^{15}$ atoms of Ag/sq.cm in a close-packed monatomic layer. It is likely that the real area of a platinum surface is appreciably greater than its apparent area, and the ratio of the accessible to apparent area has frequently been considered[4] to be about 2. If this value is assumed to be correct, the amount of silver present would correspond to a layer some 7 atoms thick.

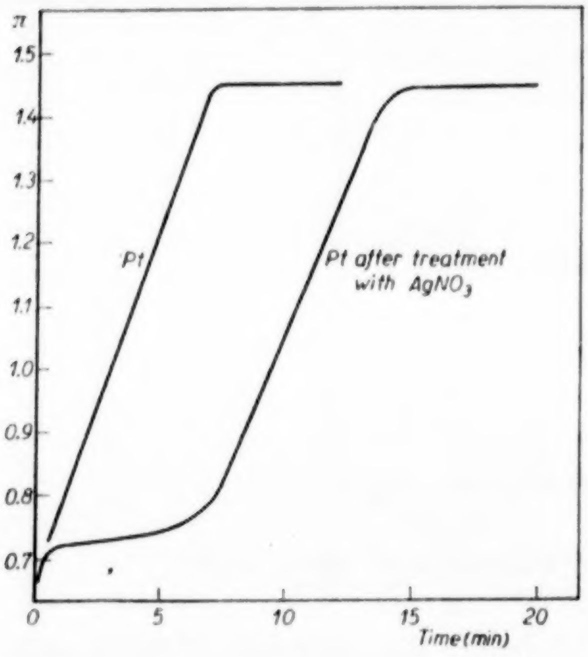

Fig. 3. Anodic charging curves.

Titration of cyanide. Titration of bromides, iodides, and thiocyanates using the platinum indicator electrode gave results very similar to those found with chloride. The titration of potassium cyanide with silver nitrate is of interest, since in the initial stages of this titration when the complex ion $[Ag(CN)_2]^-$ is being formed the simple Ag^+ ion concentration is extremely low, and it was thought that the platinum electrode might not here respond to changes in silver ion concentration. In Fig. 4 are shown some curves for the titration of 25 ml of 0.1M potassium cyanide with 0.1N silver nitrate. Curve 1 is that obtained with a platinum electrode after anodic polarization, and curve 2 after cleaning in warm concentrated nitric acid. Cathodically polarized platinum gave curve 3, while

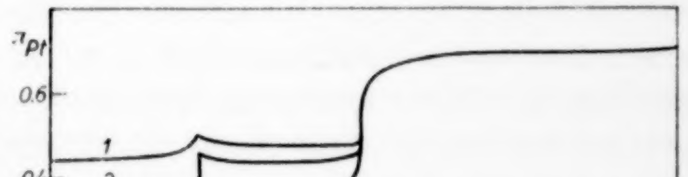

Fig. 4. Potentiometric titration of cyanide.

curve 4 was that obtained using a silver indicator electrode. The jump of potential at the first end-point is not very great with the platinum indicator electrode, and it is decreased by oxidation of the platinum surface; it is clear that in the early stages of the cyanide titration the platinum is unable to function completely as a silver electrode even after the surface has been subjected to reducing treatment. A certain concentration of silver ions appears to be necessary before the platinum indicator electrode will respond, and this concentration is higher when the platinum surface has been oxidized.

Other inert electrodes. A gold electrode after cathodic polarization was found to behave quite similarly to reduced platinum in silver nitrate/sodium chloride titrations and gave results practically identical with those found using a silver indicator electrode; a typical titration curve is graph 1 in Fig. 5. If, however, the gold surface was oxidized by anodic polarization in acid solution, or by treatment with warm concentrated nitric acid, curves 2 and 3 were obtained. Here the end-point is still indicated by a jump of potential, but all the potentials are in a higher region of 0.9 to 1.1 v which is quite removed from the normal curve.

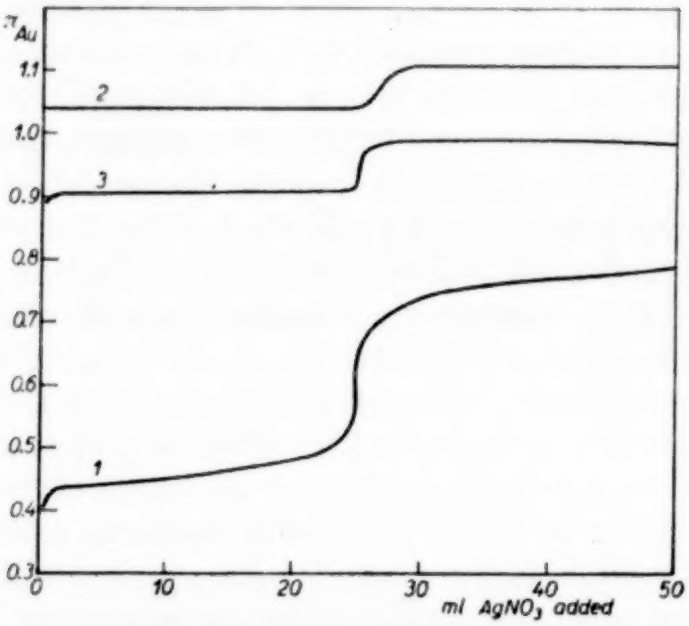

Fig. 5. Potentiometric titration of chloride with gold indicator electrode.

Electrodes prepared from battery carbon and used without any pretreatment other than washing with distilled water showed a jump in potential slightly after the true end-point in the titration had been reached, and thereafter gave potentials similar to those found with a silver electrode. The general nature of these results suggests that silver ions must be present in fairly considerable concentrations before carbon electrodes become responsive to them.

DISCUSSION

The experimental work has demonstrated that a reduced platinum surface on immersion in a solution of silver ions becomes coated with metallic silver and will then function as a silver electrode in argentometry. The formation of the silver layer is not instantaneous and an appreciable although very low concentration of silver ions is necessary for the reaction to take place. Any pretreatment which tends to oxidize the platinum surface seems to increase both the time and concentration of silver ions which is required, so that a platinum electrode thus treated does not function satisfactorily in the early stages of an argentometric titration; near the end-point, however, the concentration of silver ions is usually sufficiently great for some formation of silver to occur.

These observations can be interpreted in detail by reference to the potentials manifested by platinum after various types of pretreatment. Immediately after cathodic polarization a platinum surface is likely to be partly covered by adsorbed hydrogen, and in neutral solution this is not lost until the potential is more positive than - 0.1 v[4]. Thus, applying the Nernst equation, any solution in which the concentration of silver ions exceeds about 10^{-15} g ion per litre will tend to react with a freshly cathodically reduced platinum surface liberating metallic silver. Hence a cathodically polarized platinum electrode will behave as a silver electrode throughout almost any argentometric titration; only where the silver ion concentration is extremely low, as for example in the early stages of the titration of cyanide with silver nitrate, will it fail and even here the silver ion concentration rapidly achieves a sufficiently high value during the titration for silver formation to occur on the metal surface. A platinum surface which has been mildly oxidized is likely to be covered with platinous oxide, and the Pt/PtO potential in neutral solution is *ca.* + 0.5 v[4]; such a surface will tend to reduce any solution in which the silver ion concentration exceeds about 10^{-5} g ion per litre. Thus such a surface will not be responsive to silver ions in the early stages of many argentometric titrations and the potential will remain steady in the vicinity of the oxide potential. At or near the end-point, however, the silver ion concentration will rise sufficiently for silver to be formed on the platinum surface, and from this point onwards the electrode will behave as a silver electrode. This agrees closely with what has been observed. Drastic oxidation of the platinum surface may lead to the formation of platinic oxide, and the Pt/PtO_2 potential is *ca.* + 0.6 v[5] in neutral solution. In this case again the platinum surface will not respond to changes in silver ion concentration while this remains low, and the potential will remain close to + 0.6 v in an argentometric titration in neutral solution; when the silver ion concentration reaches about 10^{-3} g ion per litre, as for example at the end-point, the platinum will again simulate a silver indicator electrode.

Similar considerations would seem to apply to other inert electrodes. Where the potential of the surface after pretreatment is sufficiently low relative to the

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standard silver potential, then the electrode will become coated with metallic silver in the early stages of a titration and will function throughout as a silver electrode. If the potential of the surface is not low enough initially, the end-point may be reached or even slightly passed before the potential of the electrode varies with the silver ion concentration. With a sufficiently strongly oxidized surface the possibility exists that its potential may be so high that no reduction of the silver ions will occur at any stage in the titration. In this connexion the behaviour of gold after anodic polarization or treatment with warm concentrated nitric acid is of particular interest. Here the potential throughout a chloride titration is much higher than the standard silver potential (see Fig. 5) but the end-point is still indicated by a small jump of potential. After drastic oxidation a gold surface is likely to be covered by auric oxide, and the Au/Au_2O_3 potential in neutral solution is *ca.* + 1.0 v[6]; it is noteworthy that the titration curves for the oxidized gold electrode lie between 0.9 and 1.1 v. The small jump of potential of *ca.* 0.1 v at the end-point indicates that some species in equilibrium with silver ions must be formed on the gold surface, and it seems not unlikely that this might be a peroxide of silver produced by the action of auric oxide on silver ions. In support of this view a platinum electrode was anodically polarized in 0.1*N* silver nitrate so that it became coated with a black deposit which is usually considered to contain a peroxide of silver[7]; the electrode was then washed and used as an indicator electrode in the titration of 0.1*N* sodium chloride with 0.1*N* silver nitrate. The titration curve obtained was somewhat similar to that observed with oxidized gold; it lay between 1.1 and 1.3 v, there being a small jump of about 0.15 v at the end-point of the titration.

SUMMARY

A study has been made of the behaviour of platinum and some other inert electrodes in silver nitrate titrations. Where the metal surface has been subjected to a reducing treatment, such as cathodic polarization, before use, the electrode will often function as a silver indicator electrode throughout the titration. It has been shown experimentally that this is due to the formation of a layer of metallic silver upon the electrode by interaction of the surface with silver ions in solution. If the metal surface undergoes such pretreatment that it is oxidized, then its potential normally remains at the oxide value during a silver nitrate titration until the silver ion concentration is sufficiently great for this value to be exceeded by the silver/silver ion potential; formation of metallic silver then again takes place and from this point onwards the electrode behaves as a silver electrode. A detailed interpretation of the behaviour of platinum after various pretreatments has been made along these lines.

RÉSUMÉ

Une étude a été effectuée sur le comportement du platine et de quelques autres électrodes inertes lors des titrations au nitrate d'argent. Lorsque la surface métallique a été soumise à un traitement de réduction, tel que la polarisation cathodique, avant utilisation, l'électrode fonctionnera comme électrode indicatrice d'argent dans tout le cours de la titration. Il a été prouvé expérimentalement que ceci est dû à la couche d'argent métallique qui se forme sur l'électrode, par interaction entre

sa surface et les ions argent de la solution. Dans le cas où la surface du métal est soumise à un traitement préliminaire d'oxydation, son potentiel conserve normalement la valeur de celui de l'oxyde, pendant la titration au nitrate d'argent, et cela juqu'au moment où la concentration des ions argent devient suffisamment forte pour que cette valeur soit dépassée par le potentiel Ag/Ag+; à partir de ce moment, il y a de nouveau formation d'argent métallique et l'électrode se comporte alors comme électrode d'argent.

Dans cet article, les auteurs ont donné une interprétation détaillée du comportement du platine ayant subi différents traitements préliminaires.

ZUSAMMENFASSUNG

Es wird das Verhalten von Platin und einigen andern Edelmetallelektroden bei den Titrationen mit Silbernitrat untersucht. Sofern die Metalloberfläche einer reduzierenden Behandlung unterzogen wurde vor der Verwendung, wie z.B. einer kathodischen Polarisation, funktioniert die Elektrode als Silberindikatorelektrode während des ganzen Titrationsverlaufes. Es wurde experimentell bewiesen dass dies von der metallischen Silberschicht herrührt, welche sich auf der Elektrode bildet, und zwar durch die Gegenwirkung der Oberfläche mit den Silberionen der Lösung. Sofern die Metalloberfläche einer oxydierenden Vorbehandlung unterzogen wurde, behält ihr Potential den Wert des Oxydes während der Titration mit Silbernitrat, und zwar solange bis die Konzentration an Silberionen gross genug wird, um diesen Wert zu überschreiten durch das Potential Ag/Ag+. Von diesem Augenblick an bildet sich wieder metallisches Silber und die Elektrode verhält sich dann wie eine Silberelektrode. In dieser Arbeit geben die Autoren eine detaillierte Interprätation des Verhaltens von Platin, welches verschiedenen Vorbehandlungen unterzogen wurde.

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COULOMETRIC TITRATION OF ZINC WITH FERROCYANIDE

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Although many different types of electrode reactions have been utilized in coulometric titrations[1], the use of the ferri-ferrocyanide couple has not previously been reported. This couple possesses very favorable electrochemical characteristics, and is applicable to both redox titrations and to precipitation titrations of various metal ions. Because the couple functions reversibly, and because of the intermediate position of its formal potential (ranging from *ca.* +0.4 to +0.7 v *vs.* N.H.E. depending on acidity and other conditions), it is relatively easy to generate either ferrocyanide or ferricyanide ion at a platinum electrode with 100% current efficiency over a wide range of solution conditions.

In the present study a method has been developed for the titration of zinc ion with ferrocyanide ion generated by the reduction of ferricyanide ion at a platinum cathode. With the pH of the medium adjusted to between 1 and 3 the zinc precipitates as $K_2Zn_3[Fe(CN)_6]_2$, and the equivalence point is detected potentiometrically with a platinum indicator electrode. The titration may be performed manually with ordinary equipment, or more conveniently with the automatic coulometric titrator previously described[4].

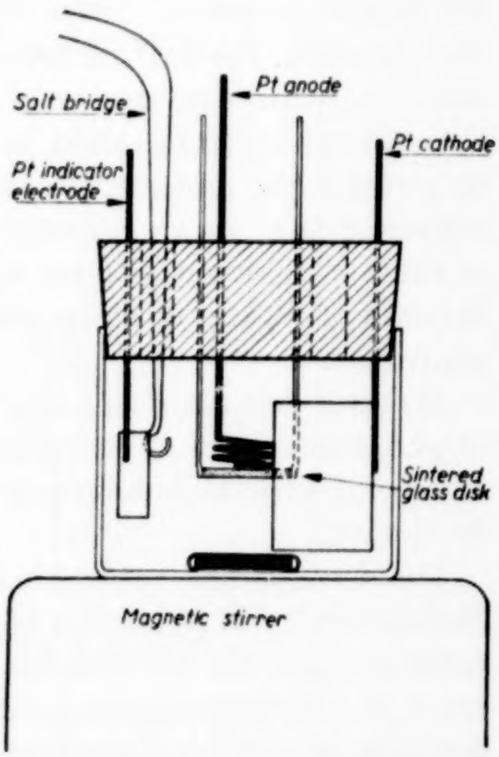

Fig. 1. Titration cell.

EXPERIMENTAL

Instrumentation. The titration cell, whose capacity was *ca.* 100 ml, is shown in Fig. 1. The cathode was a bright platinum foil (3.5 × 5 cm) bent in a circle arc to be approximately equidistant at all points from the central anode compartment, and thus to provide uniform current density. The anode was a coil of platinum

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wire, and it was isolated from the test solution by placement in the central tube whose bottom is closed by a sintered glass disk. The anolyte in this tube was approximately 1M sodium sulfate, and its level was kept above that of the test solution in the body of the cell. A piece of bright platinum foil (1 × 2 cm) served as indicator electrode. The usual type of saturated calomel reference electrode was used; it was placed in a separate small beaker and electrolytic connection to the test solution was completed by a salt bridge containing *ca.* 1M sodium sulfate. Efficient stirring was provided by a magnetic stirrer.

Titrations were performed both manually and automatically. The apparatus for manual titration employed essentially the same power supply previously described[4]. A double pole – double throw switch was placed in the electrolysis circuit. One side of this switch was used to direct the current either through the cell or through a dummy resistor whose resistance was adjusted to approximately match the cell impedance (resistance plus back e.m.f.). The other side of the switch controlled the electric stopclock used to measure the electrolysis time. The electrolysis current was measured in terms of the iR drop across a precision resistor in series with the cell with a Wolff potentiometer. The same potentiometer was used to measure the potential of the indicator electrode against the calomel reference electrode.

The apparatus for automatic titration, employing a Beckman Automatic Titrator, has been described elsewhere[4]. In the automatic titrations the constant current source described by LINGANE[5] was used; this device maintains currents of any magnitude between about 3 and 100 milliamp constant to within ±0.01% for periods of several hours. With the type of generating current supply used in the previous studies[4] optimum functioning of the Beckman autotitrator was observed when the generator electrodes were left ungrounded. However, with the current controller used in the present investigation, it was found necessary to connect the generator cathode to an earth ground through a 10 microfarad capacitor (*i.e.* an a.c. ground). Without this a.c. ground the potential readings of the Beckman autotitrator were in error by approximately 100 mv, presumably because of pickup of stray a.c. signals from the Brown amplifier of the current controller.

Reagents. Standard zinc solutions were prepared by dissolving weighed amounts of pure zinc in a small excess of dilute sulfuric acid and diluting to known volume. The volumetric technique was such that the amounts of zinc titrated were known to ±0.2%.

The ferricyanide supporting electrolyte was freshly prepared each day from Mallinckrodt AR potassium ferricyanide. Because of the instability of ferricyanide solutions, and the fact that the decomposition products consume zinc, the solutions must be freshly prepared. Even the purest commercial preparations of potassium ferricyanide contain sufficient zinc-reactive impurities to necessitate pre-titration of the supporting electrolyte to the equivalence point potential before the zinc sample is added. With 100 ml of 0.2M potassium ferricyanide (Mallinckrodt AR) the impurities caused about a 20 sec undertitration at 10 milliamp, which is equivalent to about 0.2 mg of zinc.

Titration characteristics

The titration of zinc with ferrocyanide by the classical potentiometric and volumetric techniques[2,3,6] is greatly influenced by the nature of extraneous salts present. In the present study we discovered that the pH of the solution has a profound effect on the composition of the precipitate and other characteristics of the titration. This is demonstrated by the titration curves in Figs. 2 and 3, which were obtained manually.

In all cases the supporting electrolyte contained 0.2M potassium ferricyanide, the quantity of zinc titrated was 5.22 mg, and the generating current was 29.77 milliamp. Over the pH range from 3 to 10 the solutions were buffered with 0.1M ammonium acetate, with the addition of either acetic acid or ammonia to produce the desired pH as measured by a glass electrode. The solutions of pH 1 and 2 were obtained by addition of hydrochloric acid to the potassium ferricyanide electrolyte. The generating times corresponding to the normal salt, $Zn_2[Fe(CN)_6]$, and the potassium double salt, $K_2Zn_3[Fe(CN)_6]_2$, are indicated by the vertical lines.

Between pH 1 and about 3 the inflection point corresponds exactly to $K_2Zn_3[Fe(CN)_6]_2$. With increasing pH above about 3 precipitates containing a progressively smaller proportion of ferrocyanide to zinc are formed, and when the pH is above about 6 the ratio of ferrocyanide to zinc is even smaller than

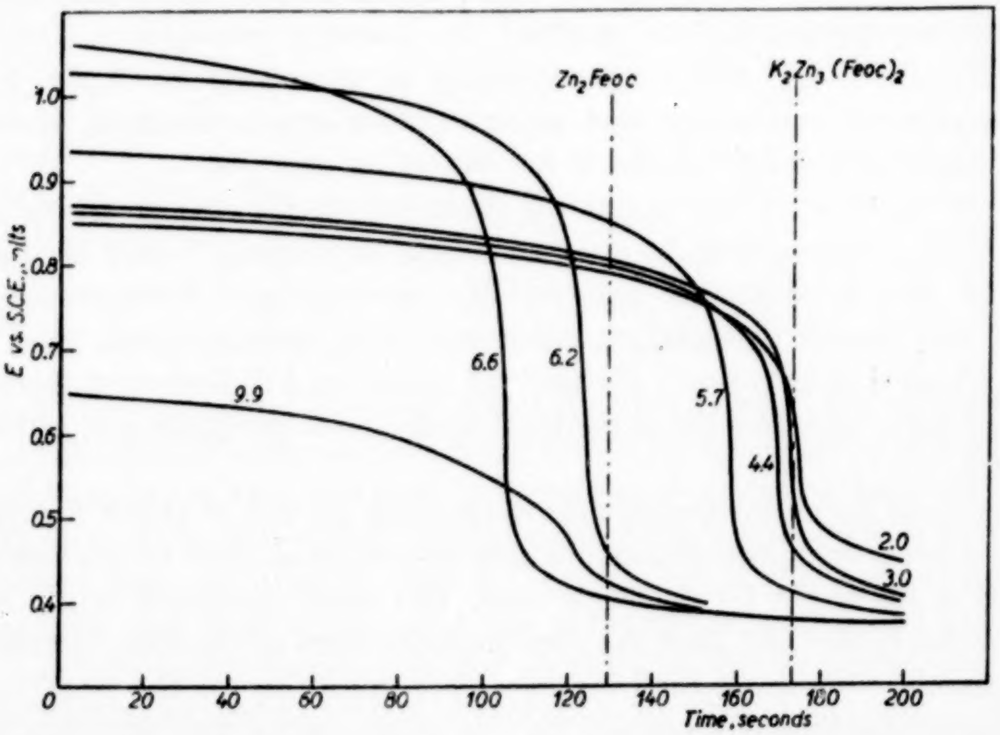

Fig. 2. Influence of pH on titration curves. The numbers for each curve are pH.

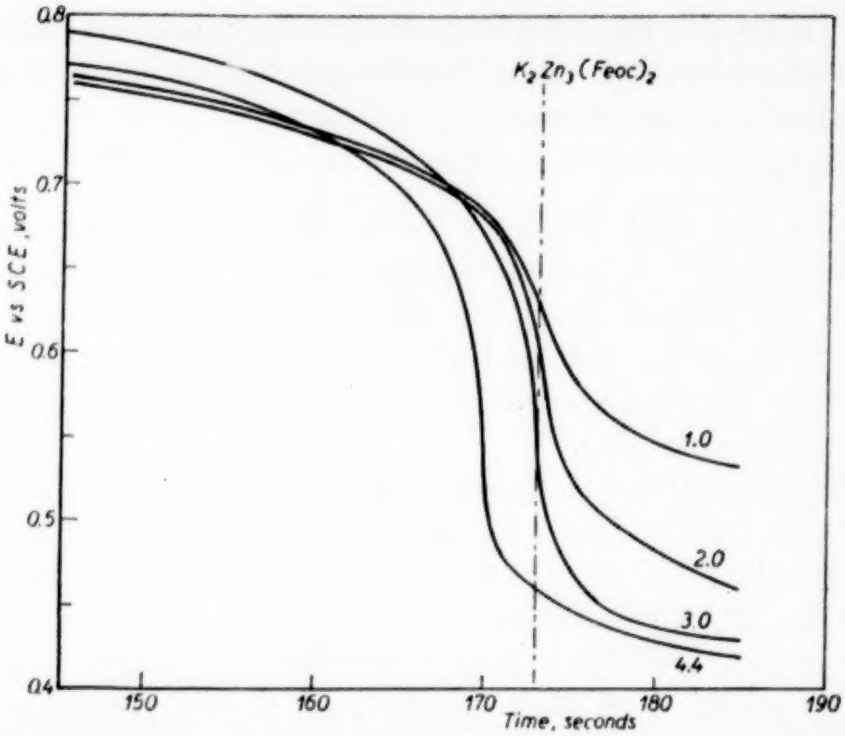

Fig. 3. Influence of pH on titration curves in immediate vicinity of equivalence point. The numbers for each curve are pH.

for the simple zinc ferrocyanide, $Zn_2[Fe(CN)_6]$. In these titrations the generating current was applied incrementalwise, and care was taken to wait for steady potential readings between increments, so that the curves correspond to equilibrium conditions.

There is evidence in the literature[3,6] that under certain conditions of titration by the ordinary potentiometric method the primary precipitate contains considerable $Zn_2[Fe(CN)_6]$, which subsequently is converted to $K_2Zn_3[Fe(CN)_6]_2$. Under the present conditions, and when equilibrium is attained, it is evident that the simple zinc ferrocyanide is not stable at any pH.

It may be noted that the upper pH limit (*ca.* 3) for the precipitation of $K_2Zn_3[Fe(CN)_6]_2$ corresponds to a pH at which $H[Fe(CN)_6]^{-3}$ and $H_2[Fe(CN)_6]^{-2}$, rather than free ferrocyanide ion, are the predominant ferrocyanide species. The third and fourth dissociation constants of hydroferrocyanic acid are 10^{-3} and $5.6 \cdot 10^{-5}$, so that at pH = 3 the ratio of mono- and di-hydrogen ferrocyanides is close to unity, and free ferrocyanide ion does not predominate until the pH exceeds 4.2.

The decreased potential break with decreasing pH below about 6 results from increasing solubility of the potassium zinc ferrocyanide due to the formation of mono- and di-hydrogen ferrocyanide ions. The small potential break at pH 9.9 doubtless reflects the fact that the predominant form of the zinc in this solution is the ammonia complex, which increases the solubility of the precipitate.

From these experiment a pH of 2 to 3 is optimum for the titration. Identical results were obtained when sulfuric acid was used instead of hydrochloric acid to acidify the ferricyanide solution, and when the concentration of potassium ferricyanide was varied between 0.05 and 0.2*M*. Under optimum conditions (pH 2 to 3, and 0.2 *M* potassium ferricyanide) the potential becomes steady quickly, whereas at pH values above about 4 potential equilibrium is reached quite slowly.

Because the titration reaction is unsymmetrical the equivalence point does not coincide exactly with the point of maximum slope. However, the rate of potential change near the equivalence point is so great that no significant error results from taking the point of maximum slope as the equivalence point. At pH = 2.0 the equivalence point potential is +0.58 v *vs.* S.C.E.

Automatic titration performance data

Table I summarizes results obtained in automatic titrations of quantities of zinc ranging from about 0.3 to 30 mg in 80 ml of a supporting electrolyte containing 0.2*M* potassium ferricyanide and sufficient hydrochloric acid to yield a pH of 2.0 ±0.1 as measured by a glass electrode.

TABLE I

AUTOMATIC COULOMETRIC TITRATION OF ZINC

Generating currents, known to ± 0.01%, ranged from 3 to 94 milliamp, and were selected to yield titration times of 100 to 600 sec

Zn taken mg	No. of Trials	Zn found Average mg	Av. error %	Av. deviation %
0.328	4	0.320	—2.4	±1.4
0.651	5	0.648	—0.5	±0.3
1.308	5	1.299	—0.7	±0.7
2.613	6	2.602	—0.4	±0.1
5.223	12	5.239	+0.3	±0.3
6.564	5	6.493	—1.1	±0.02
10.45	16	10.49	+0.4	±0.8
13.06	5	13.32	+2.0	±0.2
26.15	10	26.05	—0.4	±1.6

In all cases the supporting electrolyte was freshly prepared and was pretitrated to eliminate the effect of zinc-reactive impurities. This was done by adding a small, unmeasured quantity of zinc, in excess sufficient to require a 30 to 50 sec titration time with the particular generating current used. After waiting one or two minutes for equilibrium, the autotitrator was set to titrate to the equivalence point. The zinc sample was then added, and the autotitrator was set to titrate it as closely as possible to the same potential attained in the pre-titration.

The autotitrator was set to stop at a potential slightly in advance of the equivalence point potential, so that the final potential would lie on the steepest part of the curve. The optimum setting depends on the quantity of zinc titrated, on the magnitude of the generating current, on the geometrical properties of the cell, and on the conditions of stirring, but is very easily established by trial. With the smaller quantities of zinc the optimum setting is practically coincident with the equivalence point potential, but with the larger amounts it is as much as 100 mv in advance of the equivalence point potential. Provided that the same final potential is reached in the pre-titration and the actual titration, it is not necessary that the titrations stop precisely at the equivalence point potential. An arbitrary end-point potential may be used, but for maximal precision it should lie in the region of maximum slope.

The final potentials attained in the pre-titration and the actual titration were noted, and if there was a significant difference the proper correction was applied based on the slope of the titration curve. The correction for this ,,end-point error" was always smaller than 1 sec, and usually was considerably less.

With a given quantity of zinc the results were found to be independent of the generating current employed within wide limits. For example, in the sixteen trials with 10.45 mg of zinc the generating current was varied from 15 to 94 milliamp, and correspondingly the titration time ranged from about 650 to 110 sec, without any noticeable trend in either the accuracy or precision. The ,,anticipation control" of the autotitrator was adjusted so that about twenty incremental applications of current occurred as the end point was approached. Since the smallest final increments were *ca.* 0.3 sec, the generating current should be selected so that the titration time is not much smaller than 100 sec if maximal precision is desired.

The data in Table I were obtained by roughly matching the generating current to the quantity of zinc titrated so that the titration times were between 100 and 600 sec. Under these conditions the error is independent of the quantity of zinc titrated within wide limits, and on the average is well within ±1%. As far as we are aware successful titrations of zinc with ferrocyanide by the classical methods have not been reported with quantities of zinc as small as those in Table I.

That the small and random errors are not associated with the generation of ferrocyanide ion, but probably stem from the precipitation reaction itself, is demonstrated by titrations in which 95% of the ferrocyanide ion was generated in the solution before adding the zinc sample. These titrations agreed to ±0.5% with those performed in the usual manner, showing that the generation of ferrocyanide ion proceeds with 100% current efficiency.

The chief limitation to the smallest quantity of zinc that can be titrated is the uncertainty introduced by the pre-titration required to eliminate the effect of zinc-reactive impurities in the potassium ferricyanide. We found that recrystallization of the potassium ferricyanide decreases these impurities, but their complete removal is difficult. However, by using a smaller concentration of the potassium ferricyanide, and a smaller volume of solution, amounts of zinc considerably smaller than those we studied probably could be titrated successfully.

This method should also be applicable to the determination of the various other metals that are titratable with ferrocyanide ion by the classical techniques[3,6]. However, the optimum solution composition and pH probably will not be the same as for the titration of zinc, and will need to be established in each case.

ACKNOWLEDGEMENT

We are indebted to the Mallinckrodt Chemical Works for partial financial support of this study.

SUMMARY

A method has been developed for the automatic coulometric titration of zinc ion with ferrocyanide ion generated by the reduction of ferricyanide ion at a platinum cathode. The composition of the zinc precipitate was found to depend on the pH. Over the pH range from about 1 to 3 it corresponds exactly to $K_2Zn_3[Fe(CN)_6]_2$, but at higher pH values the precipitate contains a smaller proportion of ferrocyanide to zinc. At the optimum pH of 2 quantities of zinc from 0.3 to 30 mg in 80 ml were titrated automatically with an average error smaller than ± 1%. The ferri-ferrocyanide couple should be applicable to other coulometric titrations involving both redox and precipitation reactions.

RÉSUMÉ

Les auteurs proposent une méthode de dosage coulométrique automatique du zinc par l'ion ferrocyanhydrique, formé par réduction de l'ion ferricyanhydrique à la cathode de platine. La composition du précipité de zinc dépend du pH; aux pH de 1 à 3 environ, elle correspond exactement à $K_2Zn_3[Fe(CN)_6]_2$, mais aux pH plus élevés le précipité renferme une proportion plus petite de ferrocyanure par rapport au zinc. Au pH de 2 des quantités de zinc de 0.3 à 30 mg/80 ml peuvent être dosées automatiquement avec une erreur moyenne plus petite que ± 1%. Le couple ferri-ferrocyanure peut s'appliquer à d'autres titrations coulométriques utilisant des réactions redox ou de précipitation.

ZUSAMMENFASSUNG

Die Autoren schlagen eine Methode vor für die automatische coulometrische Bestimmung von Zink mit dem Ferrocyanidion, welches durch Reduktion von Ferricyanid an der Platinkathode entsteht. Die Zusammensetzung des Niederschlages hängt vom pH ab; bei einem pH zwischen 1 und 3 ungefähr, entspricht sie genau der Formel $K_2Zn_3[Fe(CN)_6]_2$, aber bei höhreren pH-Werten enthält der Niederschlag weniger Ferrocyanid in Bezug auf das Zink. Beim pH 2 können Quantitäten von Zink von 0.3 bis 30 mg/80 ml automatisch bestimmt werden mit einer mittleren Abweichung unter ± 1%. Das System Ferri-Ferrocyanid kann auch für andere coulometrische Titrationen verwendet werden, welchen Redox- oder Niederschlagsreaktionen zu Grunde liegen.

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POTENTIOMETRISCHE MESSUNG VON REAKTIONSGESCHWINDIGKEITEN UND VON KLEINSTEN, KATALYTISCH WIRKSAMEN STOFFMENGEN. — JODID UND KUPFER

von

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In einem der letzten Hefte dieser Zeitschrift beschreibt W. T. BINNERTS[1] Bestimmungen von Jodid in wässrigen (leicht alkalischen) Extrakten von Milchasche; er verwendet das katalytische Verfahren von SANDELL AND KOLTHOFF (Beschleunigung der Reaktion zwischen AsO_2^- und Ce^{+4}), bestimmt aber nicht die volle Reaktionszeit am Umschlagen der Eisen-Phenanthrolin-Farbe, sondern er misst das gradweise Abklingen der Ce^{+4}-Färbung in der Photometerzelle. Auf diese Möglichkeit einer beträchtlichen Verfeinerung der Messtechnik haben schon die genannten Autoren hingewiesen, und die gleiche Anregung habe ich für eine andere Bestimmung gegeben, die Kupfer-Katalyse der Reaktion zwischen Fe^{+3} und Thiosulfat[3,4].

Inzwischen hat sich nun gezeigt, dass es ein noch viel wirksameres Mittel gibt, den Verlauf derartiger Reaktionen zu verfolgen und ihre Geschwindigkeit zu messen, ein Mittel das eine mögliche Erweiterung unsrer Arbeitstechnik verspricht, vergleichbar der Überlegenheit der potentiometrischen Massanalyse gegenüber dem Arbeiten mit Farbindikatoren: Taucht man in die reagierende Lösung eine Messelektrode (Pt, Au) und den Syphon einer konstanten Bezugselektrode, so ändert sich die EMK dieser Zelle mit dem Fortschreiten der Reaktion, und dieses kann daher mit grösster Sicherheit und Genauigkeit verfolgt werden. Selbst in den Fällen, wo auch die kolorimetrische Messung möglich ist, erscheint die potentiometrische einfacher (das Potentiometer ist wohl heute in den Laboratorien noch verbreiteter als ein genaues Kolorimeter); überdies ist sie auf weit geringere Volumina, also auch Mengen anwendbar, was besonders dann von wesentlichem Vorteil erscheint, wenn Material verascht werden muss.

Das Verfahren wurde vor etwa 12 Jahren veröffentlicht[5], leider aber (Grund: Krieg usw.) an so schwer zugänglichen Stellen, dass es auch heute noch völlig unbekannt zu sein scheint; ich fasse daher hier noch einmal kurz zusammen.

Mischt man in geeigneten Verhältnissen (siehe: Versuche) die Lösung, in der Jodid bestimmt werden soll, mit Arsenit (schwefelsauer) und Ce^{IV}-salz, so misst man gegen die ges. Kalomel-Elektrode ein Potential von etwa 935 mvolt, und dieses geht beim Fortschreiten der Reaktion auf etwa 440 mvolt zurück; die

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Geschwindigkeit der Potentialänderung in verschiedenen Phasen der Reaktion und als Funktion steigender Gehalte an Jodid zeigt Fig. 1.

Sowohl für das Aufnehmen derartiger Eichkurven als auch für die darauf gegründete praktische Analyse gibt es zwei entgegengesetzte Arbeitsmöglichkeiten, die sich vorteilhaft ergänzen und die dort, wo beide gleichmässig anwendbar sind, identische Ergebnisse liefern: Verläuft die Potentialänderung langsam, so kann man die EMK in bestimmten Zeitdifferenzen messen, weil dann während des Einstellens des Potentiometers keine merkliche Potentialänderung eintritt; ändert sich das Potential sehr rasch, so ist das offenbar nicht mehr möglich, aber nun kann man statt dessen von vornherein am Potentiometer ein vorgegebenes Kompensationspotential (z.B. 850 oder 800 mvolt) einstellen, die Stoppuhr in Gang setzen, sobald die Nadel des Nullinstruments durch Null geht, dann ein niedrigeres Kompensationspotential (750 oder 700 mvolt) einstellen und die Zeit abstoppen, sobald neuerdings das Galvanometer Stromlösigkeit zeigt. Wie schon erwähnt, führen bei mittelschnellen Potentialänderungen, bei denen beide Verfahren anwendbar sind, diese zu übereinstimmenden Werten; man kann daher in Reihenversuchen mit steigenden Katalysatormengen und Reaktionsgeschwindigkeiten bedenkenlos beide kombinieren.

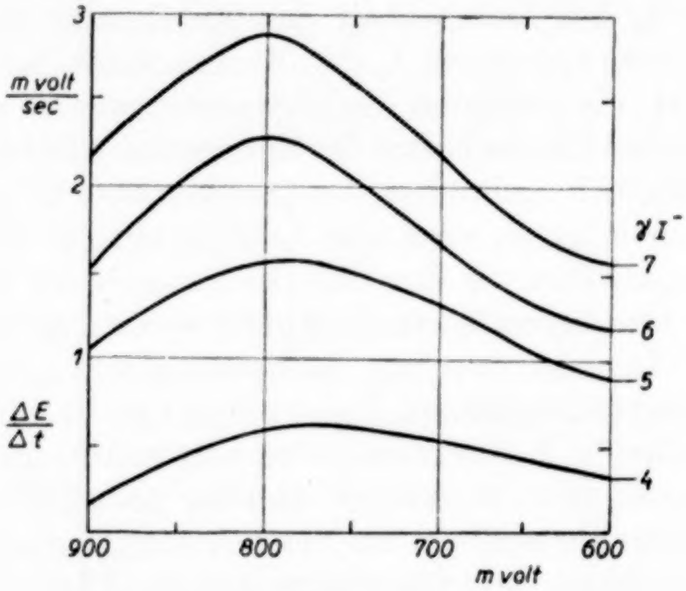

Fig. 1

Noch über die Verfeinerung und Objektivierung der Beobachtung hinaus bringt diese Arbeitstechnik einen grossen Vorteil mit sich. Schlechter noch als der Schluss der Messung, Farbumschlag oder Rückgang auf Farblosigkeit oder Farbverminderung, war bisher der Anfang der Messung definiert; von Zugabe des zweiten, die Reaktion in Gang setzenden Reagens bis zur völligen Homogenisierung der Mischung verläuft sicher eine merkliche aber variable und nicht bestimmbare Zeit, und um diese Zeit ist die gemessene Reaktionszeit unsicher; das fällt fort, wenn man als Nullpunkt ein Potential wählt, das erst einige Sekunden nach dem

Mischen erreicht wird. Es ist daher im allgemeinen ratsam, weil technisch einfacher und sicherer, in den hier aufgezeigten Fällen die Messung nicht bei 850 sondern erst bei 800 mvolt zu beginnen; man hat dann selbst bei 7 γ Jod gut 20 sec Zeit bis zur ersten Potentialgleichheit; bei 4 γ oder weniger wird man dagegen von 850 bis 750 (oder 700) mvolt messen; man hat dann am Anfang rund 1 min Wartezeit.

Ich habe schon früher dargelegt[4], dass man zweckmässig nicht unmittelbar die Reaktionszeiten t_n bei Anwesenheit der Katalysator-Menge n vergleicht, sondern den Quotienten t_0/t_n wobei t_0 die Reaktionszeit bei Abwesenheit des Katalysators bedeutet; die absoluten Reaktionszeiten werden nämlich von kleinsten Unterschieden in den Eigenschaften der Reagentien (z.B. frische oder gealterte Eisen(III)-lösung) merklich beeinflusst, der Quotient aber nicht. Den Nullwert t_0 zu messen ist aber nur möglich, wenn eine katalysatorfreie Substanz von (praktisch) gleichen Eigenschaften wie das Untersuchungsobjekt zugänglich ist. Soll der Kupfergehalt im destillierten Wasser bestimmt werden, der im Handelsprodukt stets messbar ist, so braucht man zur Bestimmung von t_0 nur eine Probe des Wassers im Glasapparat mit wirksamen Tropfenfänger zu destillieren; meist genügt es sogar, für die Nullprobe Leitungswasser zu verwenden, dessen geringer Salzgehalt die Reaktionszeit nicht beeinflusst. Soll der Jodidgehalt von Vollsalz gemessen werden, so dient als Nullwert ein Versuch mit chemisch reinem Natriumchlorid; auch hier bedingen gegenüber dem grossen Überschuss an NaCl die Spuren an Ca, Mg, Sulfat oder Phosphat keinen Fehler. Anders, wenn Jodid in Aschen physiologischer Stoffe bestimmt werden soll oder Kupfer (0.01% und weniger) in Metallen; hier ist die Herstellung einer katalysatorfreien Bezugslösung von sonst gleichen Eigenschaften sehr umständlich wenn nicht gar unmöglich. Glücklicherweise ist sie auch nicht nötig; man erhält aus einer ersten Bestimmung die Reaktionszeit t_x (und aus dieser einen grössenordnungsmässig brauchbaren Wert für die unbekannte Katalysatormenge x in der Analysenprobe), setzt in einer zweiten Bestimmung eine bekannte Menge a an Katalysator zu, am günstigsten angenähert gleich x, und erhält so t_{x+a}. Die gesuchte Menge x errechnet sich dann aus

$$Q = t_x/t_{x+a} = \frac{x+a}{x} \qquad x = \frac{a}{Q-1}$$

Die Genauigkeit wird am grössten, wenn $Q = 2$, das heisst wenn a wenigstens ungefähr gleich x ist; ist hohe Genauigkeit erwünscht, so wird man also gegebenenfalls die Bestimmung unter Zusatz von anderen, passend gewählten Katalysatormengen wiederholen. Hierin liegt eine weitere Überlegenheit der potentiometrischen Messung: Man kann bei ihr mit so ausserordentlich kleinen Lösungsmengen auskommen (deren Farbtiefe nie genau zu messen wäre), dass mehrere Wiederholungen der Messung nie an Materialmangel zu scheitern brauchen, und überdies ist die Messung so rasch und einfach durchzuführen, dass die Wiederholung nicht lästig wird.

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Fig. 2 zeigt die Ergebnisse zweier Versuchsreihen, von denen die mit den „grossen" Jodmengen, 0.2 bis 2.8 γ, bei 18°C durchgeführt wurde, die mit zehnfach kleineren aber, um die Reaktionszeiten abzukürzen, bei 90° C (Siedetemperatur des Wassers in Quito, Ecuador). In beiden Reihen wurde für die beiden niedrigsten Werte (x) der Potentialabfall in 3 min bestimmt, für die übrigen aber (o) die Zeitspanne zwischen 850 und 750 mvolt. Man sieht, wie vorzüglich die geradlinige Abhängigkeit zwischen Jodmenge und Reaktionsgeschwindigkeit (Potentialabfall), Bedingung für die angegebene Rechenweise, erfüllt ist; die Reproduzierbarkeit ist dabei so gut, dass für den Mittelwert aus drei Versuchen, die zusammen etwa 10 min beanspruchen, ein Fehler von höchstens ± 0.3% des gefundenen Wertes einzusetzen ist.

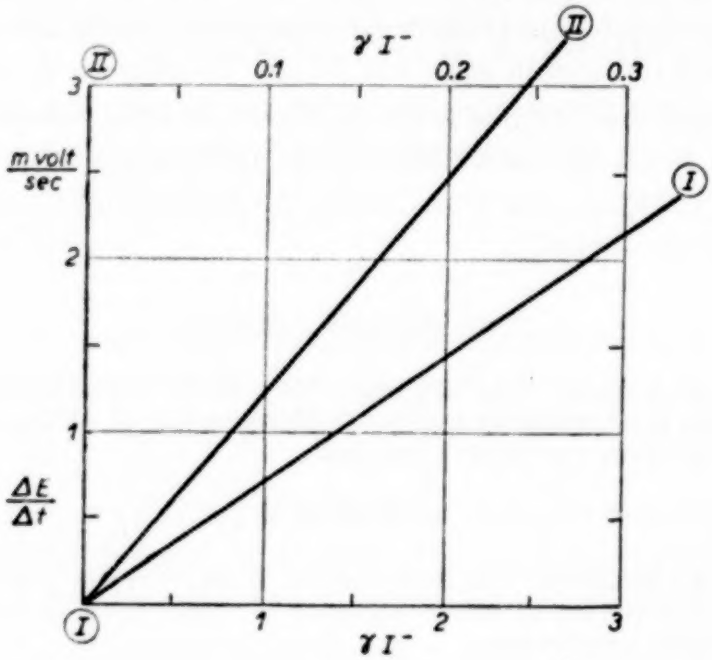

Fig. 2

Lösungen:	konz.	verd.
NaCl, in Wasser	200	50 mg/ml
Arsenige Säure, in 1.2N H_2SO_4	N/10	N/100
Cer(IV)-ammonium-sulfat, idem	N/10	N/100
Kaliumjodid, in Wasser = I^-	10	1 γ/ml

Zur Dosierung der Jodidlösung dienten Wägebüretten[6], für die übrigen Lösungen Messpipetten; sehr zweckmässig sind hierfür die automatische Messpipetten mit kapillarer Verengung an den Marken, die leicht in geeignetem Mass herzustellen sind[7].

Reihe I. Die konzentrierten Lösungen:
1 ml NaCl = 200 mg mit 0.2 — 2.8 γJod.
0.24 ml As, dann 0.1 ml Ce.
Versuchstemperatur: 18° C.

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Reihe II. Die verdünnten Lösungen:

1 ml NaCl = 50 mg mit 0.02 — 0.23 γ Jod zunächst zur Trockne verdampft, der Rückstand dann gelöst in 0.24 ml As und 0.1 ml Ce zugegeben.

Versuchstemperatur: 90° C.

Es ist einleuchtend, dass so kleine Volumina kaum kolorimetrisch beobachtet werden können, während sie zum Einführen einer Platinelektrode und des fein ausgezogenen Syphons der Kalomelelektrode völlig ausreichend sind. Rührung erfolgt zweckmässig durch einen feinen Kohlensäure-Strom, den man in einfachster Weise völlig rein erhält, indem man ein Stück Trockeneis in einem Reagensglas mit fein ausgezogenem Ableitungsrohr in Watte packt; Einsetzen in ein Dewar-Gefäss vermindert noch die Gasentwicklung. (Ein Kipp'scher Apparat mit den nötigen Reinigungsgeräten, war mir damals nicht zugänglich; selbst wo er es ist, bietet er kaum einen Vorteil.)

ZUSAMMENFASSUNG

Durch potentiometrische Verfolgung des Reaktionsablaufs katalysierbarer Reaktionen kann die Bestimmung kleinster Mengen katalytisch wirksamer Stoffe in einfacher Weise erheblich verfeinert werden.

SUMMARY

The progress of a catalysed reaction can be observed by potentiometry; by this means very small quantities of catalysts can be measured in the simplest manner and with considerable precision.

RÉSUMÉ

En suivant potentiométriquement une réaction de catalyse, il est possible de doser, très simplement et avec une extraordinaire précision, de très faibles quantités de catalyseur.

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THE POLAROGRAPHIC DETERMINATION OF MICROGRAM QUANTITIES OF OXALIC ACID

by

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INTRODUCTION

During the course of some recent work it became necessary to provide a simple and rapid method for the determination of small quantities of oxalic acid down to a concentration of 10 microg per ml in the presence of approximately 1*M* ammonium nitrate.

A survey of the literature showed that there were no methods directly applicable and few likely to be suitable for modification. The methods involving the formation and measurement of red colour with sulphosalicyclic acid, ferric chloride and lanthanum nitrate[1, 2] and those involving the interference by oxalic acid with the colour formation of the zirconium-alizarin, ferric-ferrocyanide or ferric-thiocyanate systems were not investigated. Those involving the reduction of oxalic acid to glyoxalic acid, followed by the formation of a blue colour with resorcinol in sulphuric acid[3] or a red colour with phenylhydrazine[4], and that in which reduction to glycollic acid is followed by the development of a red colour with 2:7-dihydroxynapthalene[5, 6, 7] were found to be insufficiently sensitive and not easy to carry out successfully. Treatment with resorcinol in basic solution after reduction of the oxalic acid to glyoxalic acid[8] produced a visible fluorescence from solutions within the desired concentration range, but this could not be properly examined because a sufficiently sensitive fluorimeter was not available.

Two other methods were attempted, one consisting of the precipitation of oxalic acid as calcium oxalate with subsequent dissolution in sulphuric acid and microtitration against permanganate, and the other depending on the absorptiometric determination of unreduced permanganate after the addition of sulphuric acid and excess permanganate to oxalic acid solutions. In the former case, although quantitative results were obtained in the concentration range 200-100 microgram per ml a precipitate was not obtained at lower concentrations. In the latter case consistent results were not achieved.

In view of the unsatisfactory nature of these results an investigation was made into the possibility of developing a polarographic method. It has been reported[9] that oxalic acid gives a reduction step in an ammonium chloride base electrolyte. We were not able to confirm this, nor was it possible to obtain a polarographic reduction in any other common base electrolyte. An investigation of the polarography of oxalic acid in the presence of a known concentration of ferric ions indicated that a considerable excess of oxalate was essential to the formation of good ferric waves, and the results obtained could not be related to small variations of oxalate concentration. It was, therefore, finally decided to examine the possibility of precipitating the oxalic acid with a suitable reagent, determining the unprecipitated excess of this reagent polarographically. In spite of the expense involved, europium was chosen as the precipitant because not only is the solubility product of europium oxalate low, but also europium was known to have very satisfactory polarographic characteristics.

EXPERIMENTAL

Preliminary

The polarography described in this paper was carried out at 25° C on a Cambridge photographic-recording polarograph using a dropping mercury electrode with $m^{2/3} t^{1/6} = 2.71$. The mercury pool was used as anode and all results are quoted on the European Sign convention versus the mercury pool. On this convention the potential of the Saturated Calomel Electrode (S.C.E.) has been taken as +0.246 volts versus the Normal Hydrogen Electrode (N.H.E.).

A standard europium solution was prepared by dissolving 0.0145 g "Specpure" europium oxide in 2.0 ml 10*M* hydrochloric acid and diluting to 10.0 ml with water. This solution, suitably diluted, was used for all the present work, but in view of the high cost of the material all residues were retained and the europium was recovered by the following method. The residue solutions were bulked and evaporated to small volume, neutralized to methyl orange (pH about 4), heated to boiling and treated with excess ammonium oxalate solution. The solution was then made neutral to methyl red by the addition of ammonium hydroxide, and allowed to stand for 12 hours to complete the precipitation of europium oxalate, which was filtered off on a Whatman No. 40 filter paper. The residue was washed 5 times with cold 0.1 per cent ammonium oxalate solution and then dissolved in the minimum volume of 5*M* hydrochloric acid, followed by suitable dilution and repetition of the precipitation procedure.

The final filter paper and residue were ashed to constant weight in a muffle, the yield of europium oxide showing a recovery of about 90 per cent.

Polarography of europium

The polarographic characteristics of europium were checked as follows: — 0.1 ml of the standard europium solution was placed in a 5 ml graduated flask. The pH was adjusted to about 4 by neutralization to methyl orange with dilute ammonium hydroxide, and the solution was made up to volume with water. An aliquot of this solution was transferred to a polarographic cell, deoxygenated and polarographed, the step obtained (Fig. 1) being well-shaped and having half-wave potential —0.77 volts versus the mercury pool.

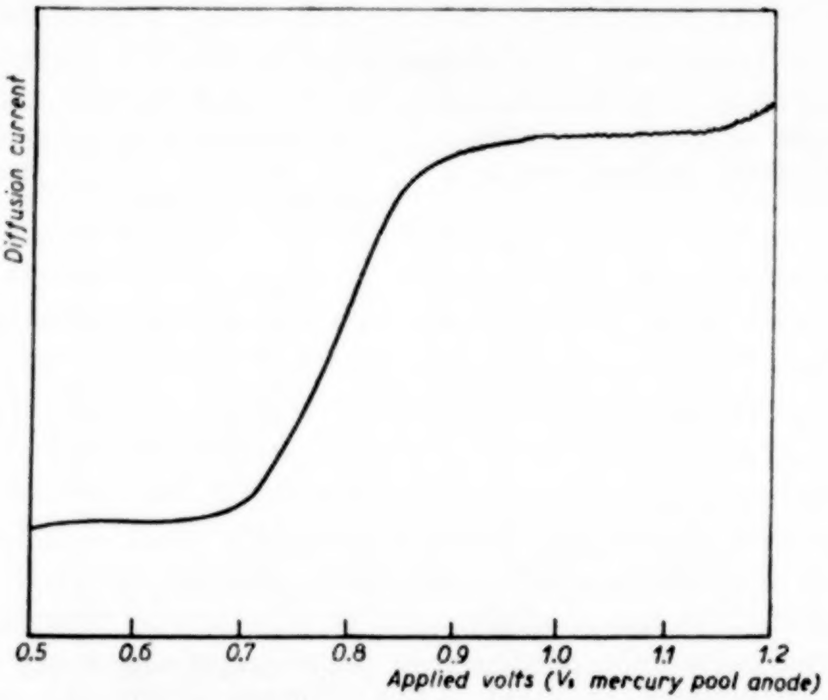

Fig. 1. 25 μg/ml europium in hydrochloric acid (pH = 4).

The effect of oxalic acid

The effect of the oxalic acid upon the europium step height was investigated by polarographing a series of solutions, prepared as described above but with 0, 25, 50, 75, 100 and 125 microg of oxalic acid added to the 5 ml flasks (*i.e.* concentrations of 0, 5, 10, 15, 20 and 25 micrograms per ml in the cell solutions).

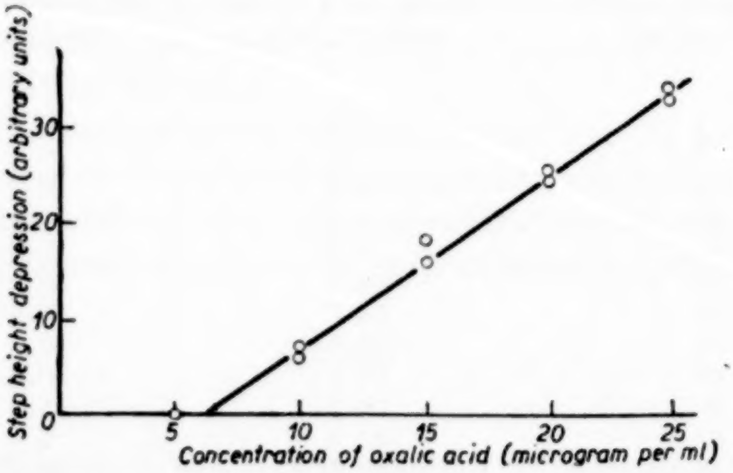

Fig. 2. Effect of oxalic acid on the europium step height (calibration graph).

References p. 494

The results obtained are given in Table I and have been employed to prepare the calibration curve shown in Fig. 2. This curve shows that the relationship between oxalic acid concentration and the depression of the europium step height is linear and that the height of the step is unaffected by concentrations of oxalic acid below 6 microgram per ml.

TABLE I

Oxalic acid concentration micro g/ml in final solution	Europium step height* (arbitrary units)	Step height depression
0	42.5	0
5	43.0	0
10	36.5	6.0
10	35.5	7.0
15	24.5	18.0
15	25.5	17.0
20	18.0	24.5
20	17.5	25.0
25	10.0	32.5
25	9.5	33.0

* All determinations were carried out on polarograph sensitivity setting 1/3. On this setting 1 scale division is equivalent to a diffusion current of $1.34 \cdot 10^{-2}$ microamp.

In order to test reproducibility a further series of solutions was prepared and investigated. In some of these ammonium nitrate was added in concentrations up to 1*M* so that the effect of this compound on the results obtained could be studied. These results are given in Table II, the recoveries being determined from the calibration graph already prepared (Fig. 2).

TABLE II

Oxalic acid added (microg/ml)	Oxalic acid found (microg/ml)	Ammonium nitrate concentration
5	<6	0
6	<6	0
10	9.8	0
10	9.7	0.2*M*
10	9.7	1.0*M*
15	14.6	0
15	14.2	0.5*M*
20	19.7	0
20	19.4	0.2*M*
20	19.3	1.0*M*
25	24.5	0
25	24.2	0.75*M*

Interfering elements

No detailed survey was made of the elements likely to interfere with this determination. However, as the presence of iron and chromium in some routine sample solutions was considered possible the effect of these elements was examined. It was found that both of them, but especially chromium, interfered seriously and that their absence was essential for satisfactory determination of the oxalic acid. Many unsuccessful attempts at the separation of iron and chromium from small quantities of oxalic acid were made and in the course of the work it was shown that both elements formed with oxalic acid, cationic, anionic and neutral complexes having a wide range of composition.

In particular the following methods of separation were attempted:

(a) Precipitation of iron and chromium as hydroxides, using several variations of the standard procedure. It was found that some oxalic acid was always lost by adsorption even when sodium hydroxide was used as the precipitant with the object of keeping the oxalic acid in solution as sodium oxalate.

(b) Removal of the iron and chromium from solution by means of an ammonium form ion exchange resin. It was not found possible to remove chromium without loss of oxalic acid and, in addition, the polarographic characteristics of the solution were so altered that poor europium waves were obtained even when chromium was absent. This appeared to be due to a decrease in the hydrogen overvoltage.

(c) Employment of a "Deacidite F" ion exchange column to retain the oxalic acid while allowing the iron and chromium to pass through. The column would hold up to about 96 per cent. of 10 ml $N/10$ oxalic acid in the absence of chromium, but if it was present about 90 per cent. of the oxalic acid passed through, while chromium was visibly retained on the resin. The effect of iron was similar.

(d) Cupferron extraction of the iron from the sample solutions. It was found that the oxalic acid was lost in the ether extraction of the precipitate and excess reagent. The fact that no loss occurred in the absence of iron indicated that it was caused by adsorption or complex formation and not by solution of the oxalic acid in the ether.

In the course of the experiments it was shown that barium could be tolerated up to a concentration of $0.1M$ and that the determination could be satisfactorily carried out in the presence of very high concentrations of magnesium. In the latter case it was necessary to prepare a fresh calibration graph.

METHOD

Procedure

Place a suitable volume of the sample solution (*Note* 1) in a 5 ml graduated flask and add 1 drop of methyl orange. Run in $N/100$ ammonium hydroxide

(*Note* 2) until the colour of the solution just changes to yellow. Add 0.1 ml of a standard europium solution (*Note* 3) and make up to volume with water. Allow to stand in a thermostat bath at 25° C for 15 minutes.

Transfer an aliquot to a polarographic cell, deoxygenate the solution for 10 minutes by passing hydrogen or nitrogen gas through it and record a polarogram at 25° C over the range −0.4 volts to −1.1 volts versus the mercury pool. Measure the height of the europium step, which occurs at about −0.8 volts, and determine the oxalic concentration of the sample by reference to a calibration curve prepared as already described (Fig. 2).

Notes

1. The volume of the aliquot of sample solution should be adjusted so that the amount of oxalic acid introduced into the flask is between 50 and 125 micrograms.
2. This concentration of ammonium hydroxide solution is used on the assumption that the acidity of the sample solution is low. If this is not the case the concentration should be adjusted accordingly.
3. The standard europium solution should be prepared as follows:–

Weigh out 0.0145 g of europium oxide (the purest available) and dissolve it in 2.0 ml of $10M$ hydrochloric acid. Transfer the solution to a 10 ml graduated flask and make up to volume with water when:–

1 ml = 25 microg Eu

ANALYSIS OF SAMPLES

In order to test the accuracy and reproducibility of the method triplicate determinations were made on sample solutions of known oxalic acid content. All these solutions contained ammonium nitrate in various concentrations up to $1M$. The mean results are given in Table III below.

TABLE III

Sample	p.p.m. oxalic acid		Recovery
	Present	Found	(%)
1	22	22.1	100.5
2	25	24.6	98.5
3	55	53.0	96.4
4	110	106.5	96.8
5	96	97.0	101.0
6	20	19.1	95.5
7	25	26.2	104.8
8	180	178.5	99.2
9	76	72.8	95.7

DISCUSSION

The solution prepared as described under "Polarography of Europium" has a final concentration of ammonium chloride of 0.04*M*. The potential of the mercury pool in contact with this concentration of chloride, assuming the activity coefficient of 0.04*M* ammonium chloride to be 0.79[10], was calculated as +0.11 volts *versus* S.C.E. The measured half-wave potential for the Eu reduction of −0.77 volts *versus* the mercury pool is therefore equivalent to −0.66 volts *versus* S.C.E., which is in good agreement with the value of −0.67 volts quoted by LAITINEN AND TAEBEL[11]. Exact comparison with the E° value of −0.676 volts *versus* S.C.E. obtained by McCOY[12] for the couple $Eu^{+3} + e^- \rightarrow Eu^{+2}$ has not been possible as no figure for the solubility of europium in mercury appears to be available.

Applying the Ilkovic equation to the data it may be calculated that the diffusion coefficient of the trivalent europium ion is approximately $0.45 \cdot 10^{-5}$ cm^2.sec^{-1}, which is of the expected magnitude.

The results given in Table I and Fig. 2 indicate that the solubility of europium oxalate is equivalent to 6 microgram oxalic acid per ml. Neglecting activity coefficients this gives an approximate value of K (europium oxalate) of $8.5 \cdot 10^{-21}$. As a final volume of 5 ml was necessary the minimum amount of oxalic acid which could be detected was about 35 microgram, a figure which could easily be reduced by the use of microtechniques and micropolarographic cells.

Examination of the recoveries given in Table III indicates that the overall accuracy is likely to be better than ± 3 per cent. over most of the concentration range.

The method requires fairly careful temperature control, so that solubilities shall not be affected, and the pH of the working solutions should be within the range 3.5 ± 0.5. Excess of neutral salt has surprisingly little effect.

ACKNOWLEDGEMENTS

Acknowledgement is made to the Chief Scientist, British Ministry of Supply for permission to publish this paper. The authors also wish to thank Mr. D. A. CHARMAN for his advice throughout the work.

SUMMARY

A brief critical summary of possible methods for the determination of micro quantities of oxalic acid in solution is presented, and details are given of a satisfactory polarographic procedure for the determination of this material down to a level of 10 microg per ml in the final solution. This method involves the adjustment of the pH of the sample solution, followed by precipitation of the oxalic acid as europium oxalate. The excess europium is then determined polarographically. The method is applicable in the presence of 1*M* ammonium nitrate and in the presence of ammonium salts of other common acids. Iron and chromium interfere and must be absent.

RÉSUMÉ

Un bref compte-rendu des méthodes de dosages de micro-quantités d'acide oxalique, en solution, est présenté. Une méthode polarographique est proposée pour la détermination de l'acide oxalique jusqu'à 10 μg/ml. Ce procédé comprend la fixation du pH de la solution à analyser et la précipitation de l'acide oxalique comme oxalate d'europium. L'excès d'europium est dosé par polarographie. Cette méthode est applicable en présence de nitrate d'ammonium 1*M* et en présence d'autres sels d'ammonium. Le fer et le chrome gênent et doivent être absents.

ZUSAMMENFASSUNG

Es wird eine kurze Übersicht gegeben über die Bestimmungsmethoden für Mikroquantitäten von Oxalsäure in Lösung. Eine polarographische Methode wird vorgeschlagen für die Bestimmung von Oxalsäure bis zu 10 μg/ml. Diese Methode besteht in einer Festlegung des pH der zu untersuchenden Lösung und im Niederschlagen der Oxalsäure als Europiumoxalat. Der Überschuss an Europium wird polarographisch bestimmt. Diese Methode ist anwendbar in Gegenwart von Ammoniumnitrat 1*M* und von andern Ammoniumsalzen. Eisen und Chrom stören diese Bestimmung und dürfen nicht in der Lösung verbleiben.

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BOOK REVIEWS

Spot Tests (4th Edition) by F. FEIGL. Elsevier Publishing Company, Amsterdam, 1954.
Volume I, *Inorganic Applications*, xii + 518 pp., 44 fig., 45*s*;
Volume II, *Organic Applications*, xv + 436 pp., 68 fig., 37*s*.6*d*.

This new edition of Professor FEIGL's *Qualitative Analysis by Spot Tests* should receive world-wide acclamation. Volume I on *Inorganic Applications* retains the arrangement of material met with in the third edition, although typographical changes have been necessary to save space and thus allow of the incorporation of much new material. It is felt, however, that these changes have definitely enhanced the appearance of the pages, and the more detailed descriptions of some of the colour tests and formulation of the reactions are particularly welcome. Another new feature in the now familiar text is the incorporation of the references in separate sections at the end of each chapter. This also makes for neatness without creating any undue difficulty in locating the references, for a small note at the foot of each page enumerates the pages where these are to be found. Once more the text contains many tests which have been evolved by the author and his co-workers, and which have not been previously published. (Chapter 3 has over 20 references to the author's unpublished studies.)

Chapter 2 on the technique of spot testing is contributed by Professor PHILIP W. WEST who is himself a well-known authority on this subject, and he has also collaborated with the author in writing the introductory chapter on the development, present state and prospects of inorganic spot test analysis. These introductory chapters are followed by detailed ones on individual tests for the metals. These are sub-divided according to the reaction of the metal ions with sulphide ion, ammonium carbonate, etc. Anions are dealt with in a separate chapter and this is followed by sections on testing for free elements (metals and non-metals) and the systematic analysis of mixtures by spot reactions. The final chapter on the application to tests of purity, examination of technical materials and minerals has been considerably expanded and includes much valuable information. The book concludes with a tabular summary of the various tests giving the limits of identification and the page number where details may be found. The bibliography of the technical applications of spot reactions has been omitted from this section and this is a feature which will be missed by many users of the previous editions.

Dr. OESPERS's translation of the text flows smoothly, and he is to be congratulated on his excellent rendition. A valuable feature which is somewhat more in evidence in this edition than in previous ones is the author's suggestions on the mechanisms of some of the more complicated or less obvious reactions. These clear up many difficult points and are a veritable mine of information. It is almost certainly true to say that no analytical chemist, with the exception of the author himself, is likely to pick up this authoritative text on inorganic spot tests without deriving some new insight into their chemistry and also a sense of inspiration, for the enthusiasm of the author for his subject can be felt in every page.

Volume II on *Organic Applications* is a new departure in spot test analysis and should prove to be indispensable to organic chemists. There is no doubt that there is a great need for the spot test in qualitative organic analysis and equally there can be little doubt that this encyclopaedic compilation by the author will herald a much more widespread use of the technique .It is equally probable that the book itself and the spirit in which it has been so carefully written and arranged, will promote much interest and the evolution of many new tests. This volume does not form a supplement to Volume I but is complete in itself. It includes the introductory chapter on technique written by Professor PHILIP W. WEST for Volume I and incorporates tests for inorganic materials likely to be found in the residues after decomposition of organic samples. Whilst this treatment leads to duplication of subject matter in the two volumes, it should be stressed that the author has been concerned with the evolution of Volume II as a separate entity.

After a chapter on exploratory tests such as those for revealing the presence of halogens, sulphur, oxygen etc. in the sample, the text goes on to deal with the detection of characteristic (functional) groups in the organic compounds *e.g.* reactive CH_2 and NH_2 groups, 1,2-dicarboxylic acids, thioketones, *o*-hydroxyaldehydes, etc. and this is followed by a chapter on the identification of individual organic compounds. The book closes with a chapter on the applications of spot reactions for special technical and scientific purposes and a tabular summary of the limits of identification of the various tests detailed in the text. The same reference and index system is used as in Volume I and the same neatness in presentation is noteworthy.

Both volumes are neatly bound in limp covers with attractive wrapper designs and the excellent production and moderate price are a credit to the publishers.

T. S. West (Birmingham)

Electroanalytical Chemistry, par **James J. Lingane**. Interscience Publishers, Inc., New-York, London, 1953. 458 pages, 107 Fig., 16 tables. Prix: 68*s*.

Le but initial de l'auteur était de faire un livre sur les dosages électrolytiques à potentiels contrôlés et sur les titrations coulométriques. Lors de l'élaboration de son ouvrage, le Professeur Lingane s'est vite rendu compte qu'il n'était pas possible d'exposer avec clarté un tel sujet sans avoir préalablement posé les bases théoriques sur lesquelles repose toute l'électroanalyse. C'est ainsi que l'auteur fut conduit à traiter cette discipline dans son ensemble, exception faite toutefois pour la polarographie que le Prof. Lingane n'a pas traitée, car il existe plusieurs livres spécialisés sur cette méthode.

En quelque 150 pages, constituant les 9 premiers chapitres, l'auteur expose de façon claire et en termes précis, les notions fondamentales du potentiel, de l'intensité et de pH. Chaque expression est soigneusement définie et certains points qui sont encore l'objet de confusion dans la littérature, sont étudiés à fond.

Rappelons les principaux chapitres de cet ouvrage: Measurement of the E.M.F. of Galvanic Cells, Interpretation of the E.M.F. of Galvanic Cells, pH and its Measurement, Potentiometric Acid-Base Titrations, Potentiometric Precipitation Titrations, Potentiometric Oxidation-Reduction Titrations, Automatic Potentiometric Titrations, Conductometric Analysis, Electrolysis, Electrical Instrumentation for Controlled Potential Electrolysis, Methodology of Controlled Potential Electrogravimetric Analysis, Controlled Potential Electrogravimetric Analysis Procedures, Controlled Potential Electrolytic Separation of Metals Prior to other Determinative Methods, Internal Electrolysis (Spontaneous Electrogravimetric Analysis), Electrographic Analysis, Controlled Potential Coulometric Analysis, Coulometric Titration with Constant Current.

Le livre du Professeur Lingane, grand spécialiste en cette matière, est en tous points remarquable, tant par la clarté de l'exposé que par la façon dont les chapitres s'enchaînent et par la logique du plan adopté. Remarquable instrument de travail pour les chimistes, précieux livre de base qui rendra les plus grands services aux étudiants et aux chercheurs.

D. Monnier (Genève)

Substances naturelles de synthèse, Volume VIII, par MM. A. ALLAIS, J. MATHIEU, A. PETIT, P. POIRIER, L. VELLUZ. Ouvrage de 157 pages et 1 planche hors-texte de microphotographies. Paris, Masson et Cie. 1954. Prix: 1800 fr. broché; 2200fr. cartonné toile.

Le présent volume qui continue la tradition des sept précédents, traite des importants chapitres relatifs à l'acide nicotique, à l'acide DL-tuberculostéarique, au dicoumarol, à l'hydroxycortisone, au nicotamide, à la tryptamine et au DL-tryptophan(n)e. Les méthodes générales de travail comportent cette fois, la réduction par les hydrures mixtes et la synthèse des acides gras saturés. L'ouvrage se termine par une note pratique sur la préparation de l'hydrure d'aluminium-lithium, de l'hydrure de bore-lithium et l'hydrure de bore-sodium.

Le tableau annexé indique une vue d'ensemble des réactions faites jusqu'ici avec l'un ou l'autre de ces hydrures, avec le produit de départ, le produit final et la bibliographie naturellement très récente. On trouve encore au gré du texte des notes relatives à la préparation des organo-cadmiens, à la réaction de BOUVEAULT ET BLANC, aux synthèses par électrolyse suivant KOLBE. La note de la page 45 résume nos idées actuelles sur la conformation des molécules présentant l'isomérie chaise-cuvette; toutefois, l'apport de l'absorption infrarouge à cette importante question semble avoir été passé sous silence.

L'ouvrage est fort bien présenté. La lecture des deux articles principaux: acide nicotique et acide tuberculostéarique demeure très attachante. Déjà, on nous annonce la cystéine, la cystine et l'acide β-indolylacétique ainsi que la préparation des substances biologiques marquées et le tome X est en préparation . . .

C. DUVAL (Paris)

Wasserbestimmung mit Karl-Fischer-Lösung, by ERNST EBERIUS. Verlag Chemie, Weinheim/Bergstr., 1954. 138 pages, 38 fig., 83 tables, DM 12,80.

In accordance with the fact that KARL FISCHER's titrimetric method for the determination of water has won universal acclaim, in particular since the American workers have demonstrated its practical possibilities, the *Angewandte Chemie*, which published KARL FISCHER's article on the method in 1935, has together with the *Chemie-Ingenieur-Technik* issued a monograph which gives a summary of the execution of the titration and its chemistry, and its use in inorganic, organic and many branches of technical chemistry. This monograph is neither so comprehensive nor so thorough as MITCHELL AND SMITH's *Aquametry*—and does not afford such a fundamental and independent contribution as the American work. Within the more modest framework of this book the author has been successful not only in finding room for a well written account of the many fields in which the method can be used, but also for many practical instructions and to indicate difficulties which can be encountered when using this method.

F. REIMERS (Copenhagen)

Gegenstromverteilung, von H. M. RAUEN UND W. STAMM, mit 65 Abbildungen. vii und 81 Seiten. Springer-Verlag, Berlin, Göttingen, Heidelberg, 1953, DM 12.80. (*Anleitungen für die chemische Laboratoriumspraxis*, Band VI).

Die Trennung durch Verteilen zwischen zwei Lösungsmitteln hat in den letzten Jahren in immer steigendem Maße neue Anwendungen gefunden und die Methodik ist von vielen Seiten weiter entwickelt worden. So ist es zu begrüssen, dass die Grundlagen des Verfahrens, die wichtigsten Apparaturen, die verschiedenen Arbeitsweisen und — in knapper Form — die rechnerische Behandlung der multiplikativen

Verteilung in einer Monographie behandelt werden. Entsprechend dem Titel der Sammlung, in deren Rahmen das Buch erschienen ist, werden nur die für das Laboratorium geeigneten Methoden, nicht die technischen Anwendungen des Verfahrens beschrieben. Zum Schluss werden als Beispiele Arbeitsvorschriften für 12 Fälle, zumeist Probleme der biologischen Chemie betreffend, wiedergegeben. Wertvoll ist das etwa 150 Zitate umfassende Literaturverzeichnis.

Der Text ist nicht in allen Teilen leicht lesbar. In Abschnitt VI wäre das Verständnis durch einige bildliche Darstellungen der Trennungsschemata sehr erleichtert worden, zumal bei der Bezifferung auf S. 36 einige Druckfehler unterlaufen sind. Die historischen Bemerkungen sind nicht ganz zutreffend: die Verdienste L. C. CRAIG's um die Gegenstromverteilung sind unbestritten, aber er hat sie nicht „begründet" (Seite 2).

Der Wert des Buches liegt darin, dass es dem auf dem Gebiet der Verteilungstrennung nicht bewanderten Chemiker die Gelegenheit bietet, sich rasch einen Überblick über die durch das Verfahren gegebenen Möglichkeiten zu verschaffen.

WERNER FISCHER (Hannover)

Minerals for the Chemical and Allied Industries, par SYDNEY J. JOHNSTONE. Chapman and Hall Ltd., London, 1954, 692 pages, Prix: 75*s*.

Ce livre fort bien présenté est la réunion d'une série d'articles parus de 1946 à 1949 dans *The Industrial Chemist* et *Chemical Manufacturer* et concerne 72 corps simples ou composés rangés par ordre alphabétique. Ces corps sont étudiés sous les aspects suivants: nature des minerais, lieu de production, modes d'obtention et de purification, tonnage et surtout, les utilisations. Chaque paragraphe se termine par une bibliographie choisie relative surtout à des mémoires ou à des livres de langue anglaise. Aucune indication n'est fournie sur les caractères analytiques et les modes de contrôle de tous ces produits et il faut le déplorer, car pour certains d'entre eux, on manque souvent de renseignements. Ce livre s'adresse surtout aux utilisateurs industriels; il fourmille de renseignements précieux et donne des usages insoupçonnés souvent créés pendant la deuxième guerre mondiale. L'ouvrage se termine par un index des noms de corps cités. Sa lecture est attrayante et chaudement recommandée.

C. DUVAL (Paris)

Einschlusverbindungen, von FRIEDR. CRAMER, mit 47 Abbildungen. v und 115 Seiten. Springer-Verlag, Berlin, Göttingen, Heidelberg, 1954, DM 14.80.

Unter Einschlussverbindungen fasst man nach dem Vorschlag von W. SCHLENK eine Gruppe von Verbindungen zusammen, die dadurch ausgezeichnet sind, dass für ihr Zustandekommen vornehmlich räumliche Verhältnisse massgebend sind; die eine Komponente besitzt — in ihrem Kristallgitter oder in ihrem Molekelbau — Hohlräume, in die die Molekeln einer anderen Komponente gerade hineinpassen. Die Bindungskräfte zwischen den beiden Komponenten spielen demgegenüber eine untergeordnete Rolle. Verbindungen dieser Art bildet z.B. der Harnstoff mit unverzweigten Paraffinen und Paraffinderivaten. Es gehören hierher aber auch die Choleinsäuren und lange bekannte Verbindungen, wie die Gashydrate und die blaue Jodstärke.

Es ist sehr verdienstvoll, dass der Autor, der selbst eine Reihe experimenteller Arbeiten über diese Stoffe beigesteuert hat, im vorliegenden Werk eine ansprechende Übersicht über unsere derzeitige Kenntnis der Einschlussverbindungen gibt. Die Analogien, die er zum Vergleich heranzieht, und die Ausblicke auf die mögliche Bedeutung der neuen Verbindungsklasse für das Verständnis z.B. von Antikörpern und Fermenten mögen etwas kühn sein, machen die Lektüre aber anregend. Bei einer Neuauflage wäre die Einleitung über die chemische Bindung erheblich zu revidieren, da sie eine Reihe von anfechtbaren Formulierungen bringt. Die zwischen-

molekularen Kräfte benennt man nach VAN DER WAALS (der Druckfehlerteufel lässt dafür konsequent stets V. D. WAAL erscheinen).

Die Lektüre des vorliegenden Büchleins lohnt sich auch für den Analytiker sehr, besonders wenn er auf organisch-chemischem Gebiete arbeitet. Denn die Einschlussverbindungen gestatten manche Stoffe zu trennen, die sich auf anderen Wegen nicht oder nur sehr viel mühsamer scheiden lassen. Und es ist zu hoffen, dass die neue Verbindungsklasse gerade auf diesem Gebiet noch ausbaufähig ist.

WERNER FISCHER (Hannover)

Traité de Micro-analyse minérale qualitative et quantitative par CLÉMENT DUVAL (avec une préface du Prof. CHEVENARD). Presses Scientifiques Internationales. Paris, 1954. 552 pages, 122 figures, prix: FFr. 3.000.—.

Les très nombreux domaines de la micro-analyse minérale ont subi, au cours de ces dernières années, un essor considérable. Les publications y relatives sont si nombreuses qu'il est fort difficile de se faire une idée d'ensemble d'une si vaste discipline, l'une des plus importantes de la chimie moderne. Nous devons donc être reconnaissants au Professeur CLÉMENT DUVAL d'avoir entrepris la rédaction d'un Traité de Micro-analyse et de mettre ainsi à la disposition des étudiants, des techniciens et des chercheurs, un incomparable instrument de travail. En possession d'une documentation remarquable et de nombreux résultats expérimentaux recueillis dans ses laboratoires, nul n'était mieux qualifié que le Professeur DUVAL pour écrire un tel ouvrage.

Le tome premier vient de sortir de presse. Il traite des éléments des groupes I A, II A et III A de la table périodique et de leurs dérivés (y compris les isotopes). Chaque chapitre comprend une introduction dans laquelle l'auteur donne maints renseignements d'intérêt analytique: propriétés physiques et chimiques, état naturel, séparation, mise en solution, etc. puis une partie consacrée à l'analyse qualitative et une autre à l'analyse quantitative. A côté de techniques dites classiques, qui comprennent la gravimétrie et la volumétrie, on y trouve toutes les méthodes modernes d'analyse physico-chimique: colorimétrie, potentiométrie, polarographie, spectrographie, thermogravimétrie, etc...

Rappelons brièvement le sommaire du Tome 1 : Chapitre 1. Hydrogène — 2. Deutérium — 3. Tritium — 4. Eau — 5. Eau oxygénée — 6. Oxyde de deutérium — 7. Oxyde de tritium — 8. Lithium — 9. Sodium — 10. Potassium — 11. Rubidium — 12. Césium — 13. Francium — 14. Béryllium — 15. Magnésium — 16. Calcium — 17. Strontium — 18. Baryum — 19. Radium et isotopes. 20. Scandium — 21. Yttrium — 22. Terres rares — 23. Lanthane — 24. Cérium — 25. Praséodyme — 26. Néodyme — 27. Prométhium — 28. Samarium — 29. Europium — 30. Gadolinium — 31. Terbium — 32. Dysprosium — 33. Holmium — 34. Erbium — 35. Thulium — 36. (Béo) Ytterbium — 37. Lutétium — 38. Actinium — 39. Mésothorium-II.

La présentation de ce livre est très soignée, les dessins, fort bien réussis. Il est relié sous jaquette bleu foncé. Livre de base, renfermant une foule de renseignements précieux et des méthodes classiques modernes éprouvées au laboratoire. Chaque chapitre est accompagné d'un grand nombre de références bibliographiques.

Soulignons pour terminer que les P.S.I. livrent cet ouvrage à un prix extrêmement modique.

D. MONNIER (Genève)

Méthodes et réactions de l'analyse organique. II. Méthodes de caractérisation, publié sous la direction de LÉON VELLUZ, par M. PESEZ ET P. POIRIER, préface de CH. DUFRAISSE. Masson et Cie, Paris 1953. Un volume broché de 278 pages et 7 planches, prix: 2590 fr.

J'ai rendu compte précédemment (*Anal. Chim. Acta,* 7 (1952) 480) de la valeur du Tome 1 de cette collection; je voudrais maintenant parler du Tome II dont je suis usager depuis près d'un an. L'ouvrage est un traité d'analyse organique fonctionnelle, restreinte aux méthodes purement chimiques, c'est-à-dire qu'il traite de l'obtention et des propriétés des réactifs généraux et de la manière d'obtenir les dérivés caractéristiques en y adjoignant de longues listes de points de fusion. Le nombre de ces réactifs est voisin de 140; autrement dit, le sujet est poussé bien à fond. On sait que certains de ces réactifs sont polyvalents, qu'ils servent à caractériser plusieurs fonctions; c'est pourquoi, le plan repose plutôt sur le réactif que sur la fonction; ce n'est pas très grave à cause de l'index et de la table des matières qui sont bien complets. Le plan du volume est donc le suivant: alcoylation et arylation; acylation; urées, uréthan(n)es et allophanates; amidation; oximes et hydrazones; sels et composés d'addition; réactions diverses. Les différentes opérations qui sont des synthèses en petit, sont décrites clairement, avec les détails nécessaires; l'ouvrage peut servir non seulement au chimiste de métier, mais encore à l'étudiant, à l'élève ingénieur. On pourra peut-être objecter — et je l'ai entendu dire — que le livre ne possède pas assez le style microchimique mais, les auteurs n'ont voulu nous donner que 278 pages et si l'on voulait transposer toutes ces réactions d'identification à l'échelle de 5 mg au lieu de 0.1 g il faudrait écrire un 4ème tome et emprunter le matériel de LIEB et SCHÖNIGER. Non, les auteurs se sont fixés un objectif et ils l'ont atteint; attribuons un bon point aussi à leurs collaborateurs immédiats MM. J. MATHIEU, A. PETIT et J. WOHLGEMUTH; ils ne nous ont pas donné un ouvrage de compilation, mais ils ont effectué à travers la chimie organique un long voyage dont ils nous rapportent fidèlement leurs impressions à chaque étape.

C. DUVAL (Paris)

Méthodes et réactions de l'analyse organique III. Réactions colorées et fluorescences, publié sous la direction de LÉON VELLUZ, par M. PESEZ ET P. POIRIER, préface de CH. DUFRAISSE. Masson et Cie, Paris 1954. Un volume broché de 297 pages, prix: 2.750 fr.

Ce tome troisième fournit des centaines de réactions colorées servant à l'identification des corps organiques; ceux-ci ne sont pas rangés par ordre de complexité croissante ou dans l'ordre d'un cours classique de chimie organique. Les auteurs étudient les principes de réaction et les font suivre de la pratique des essais, par exemple: oxydation-réduction, réactifs métalliques et métalloïdiques, diazotation-copulation, formation d'imines, d'indophénols, d'arylméthanes, d'hétérocycliques, etc., de sorte que si l'on veut caractériser un aldéhyde, il faut se reporter à sept ou huit chapitres, ce qui déroute bien un peu le lecteur, au premier abord. Les limites de dilution, même celles qui sont connues, ne figurent pas malgré leur utilité incontestable. De place en place, on trouve les limites de sensibilité sous le vocable „sensibilité" et sans se préoccuper des substances qui interfèrent ou qui la diminuent. Les réactions de fluorescence sont très jolies, mais je ne sais pas si on peut les recommander sans fournir, comme l'avait fait ANDANT dans sa Thèse de Pharmacie, le spectre de fluorescence correspondant qui, lui, est un document, car très souvent, le phénomène est dû à une impureté (cas du fluorène qui ne mérite plus son nom). L'ouvrage se termine par un tableau des principales solutions utilisées comme tampon.

Malgré la richesse de documentation accumulée et l'excellente présentation, je trouve ce tome moins intéressant que les deux premiers, moins personnel, moins critique et beaucoup plus ouvrage de compilation. Sur de nombreux points, il ne tient pas compte des recommandations de l'Union internationale de Chimie, mais, je me représente très bien le travail énorme qu'il y aurait à faire pour contrôler toutes ces réactions colorées à tel point que l'Union, elle-même y a renoncé. Les tables et index d'auteurs, de réactifs et de corps identifiés sont bien dressées et suffisamment complètes. Il reste à féliciter chaudement LÉON VELLUZ et ses collaborateurs pour avoir mené à bien, en un temps relativement court, l'exécution de leur projet, pour avoir écrit un livre de chimie analytique malgré le dédain que l'on porte en France à cette science rationelle et pour avoir extrait du domaine si touffu de la chimie organique, un ensemble harmonieux qui nous rend journellement les plus grands services. Nous souhaitons à ces trois volumes un gros succès de librairie.

C. DUVAL (Paris)

THE PREPARATION OF STANDARD SOLUTIONS OF SULPHURIC ACID BY MEANS OF SPECIFIC GRAVITY DETERMINATIONS

by

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INTRODUCTION

As far back as 1905, WORDEN AND MOTION[1] published a table of specific gravities of dilute solutions of sulphuric acid, for use in preparing standard solutions. At the present time, The Association of Official Agricultural Chemists[2] advocates, as an official method, the preparation of standard solutions of sulphuric acid, by means of a formula relating the specific gravity of an approximately 70% sulphuric acid solution to its exact percentage composition by weight. This formula is derived from MARSHALL[3] and is claimed to be accurate to 1 part in 1500. MARSHALL's formula is itself based upon the density figures of PICKERING[4].

The acid of 70% strength used by the A.O.A.C. suffers from the disadvantage that it is very hygroscopic, so that special precautions must be observed in weighing it, and it is, moreover, unpleasant material to handle for a specific gravity determination. HAKE[5] showed that the maximum absorption of moisture by concentrated sulphuric acid reduces it to 35.37% by weight, so that acid of this strength or near it should show little or no hygroscopicity, and could therefore be weighed easily in open vessels. MARSHALL's formula is inapplicable to acids of this concentration. GAEHR[6], however, pointed out that the concentrations of dilute solutions are often proportional to the logarithms of their densities, and a relationship of this type was found to hold very closely for concentrations of sulphuric acid lying between 32% and 39% by weight. At concentrations higher than 39% the equation was not satisfactory.

PICKERING's figures have been criticized by DOMKE[7] on the ground that PICKERING employed a relative and not an absolute unit for his work, and that his percentages by weight are high by about 0.26% of their value. It has also been pointed out in THORPE's *Dictionary of Applied Chemistry*[8] that although the claimed accuracy of PICKERING's results is 8 parts per 1,000,000, the eight analyses of his strong acid yield a mean of 99.8495% with a range from 99.704% to 99.962%, or about 1 part in 400. The standard deviation is ± 0.09043 and the standard error ± 0.03199, *i.e.* about 320 parts per 1,000,000. It seems difficult to reconcile this uncertainty with the claimed precision. The results of DOMKE[7] do not appear to have attracted similar criticism, and have been relied on for the work here reported.

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EXPERIMENTAL

Establishment of the regression-equation

To establish the regression-equation, the whole-number percentages by weight *in vacuo* of DOMKE were transformed to percentages by weight in air at 20° C, and his corresponding figures for density *in vacuo* converted to specific gravities in air at 20° C/20° C. From these calculated results the following regression-equation was derived by the method of least squares:

$$P = 343.61\ (\log_{10} \text{S.G.}) + 0.1875 \qquad (1)$$

where P is the percentage of sulphuric acid by weight in air at 20° C, and S.G. is the specific gravity in air at 20° C, referred to water at 20° C. The percentages calculated from the specific gravities by means of this equation are given in Table I, where it will be seen that they correspond very closely with those calculated from DOMKE's figures, the difference in no case exceeding 1 part in 10,000.

TABLE I

SPECIFIC GRAVITY AND PERCENTAGE BY WEIGHT OF SULPHURIC ACID SOLUTIONS

S.G. 20° C/20° C in air, calc. from DOMKE	% w/w in air at 20° C		Diff. between DOMKE & Eq.		Normality
	Calc. from DOMKE	Calc. from Equation (1)	%	Parts per 10,000	
1.2374	31.974	31.975	+ 0.001	0.3	8.072
1.2457	32.973	32.971	— 0.002	0.6	8.380
1.2541	33.972	33.975	+ 0.003	0.9	8.692
1.2625	34.972	34.971	— 0.001	0.3	9.008
1.2710	35.971	35.974	+ 0.003	0.8	9.327
1.2795	36.971	36.968	— 0.003	0.8	9.651
1.2881	37.970	37.967	— 0.003	0.8	9.978
1.2968	38.969	38.971	+ 0.002	0.5	10.310
		Mean	— 0.00025		
		Standard Deviation	+ 0.00256		

This agreement is very satisfactory in view of the fact that according to the International Table of Atomic Weights for 1951, there is an uncertainty of ± 0.003 in the atomic weight of sulphur, due to differences in isotopic ratio, which leads to an uncertainty of 1 part in 33,000 in the equivalent weight of sulphuric acid.

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Rational atomic and equivalent weights

It has been pointed out by SCHOORL[9] that International atomic weights are based upon weighings *in vacuo*, while ordinary analytical weighings are not in general corrected for buoyancy, and that unless the latter are so corrected, "rational" atomic weights based upon air-weighings should be employed in gravimetric and volumetric conversion-factors. In some cases an error of as much as 0.1% can be introduced in this way.

For the present work, the density of barium sulphate was taken as 4.50, and that of 100% sulphuric acid as 1.8305 at 20° C. Using the 1951 International atomic weights, the rational molecular weight of sulphuric acid is 98.032 ± 0.003, and its rational equivalent weight is 49.016 ± 0.0015.

On this basis, the air-weight W of sulphuric acid of P% by weight in air required to give 1 litre of 1N H_2SO_4 is given by (2) and the normality N of a solution prepared by diluting W' grammes of P% acid to 1 litre is given by (3).

$$W = \frac{4901.6}{P} \text{ grammes} \qquad (2) \qquad\qquad N = \frac{PW'}{4901.6} \qquad (3)$$

If the International figures are used, the equations become:

$$W = \frac{4904.1}{P} \ldots\ldots (2a) \qquad\qquad N = \frac{PW'}{4904.1} \ldots\ldots (3a)$$

the difference being 5 parts in 10,000.

Similarly, the rational molecular weight of barium sulphate is 233.397 ± 0.003 which yields a factor for converting air-weight of $BaSO_4$ to air-weight of H_2SO_4 of 0.42002, differing by 4 parts in 10,000 from the International factor of 0.42018.

In the present communication, rational molecular and equivalent weights have been used throughout.

Checking the regression-equation

The accuracy of equation (1) was checked at four points between 32% and 39% of sulphuric acid, by preparing suitable dilutions of pure concentrated sulphuric acid with distilled water.

KUNZLER[10] has described five methods for the preparation of very pure sulphuric acid of known strength for use as a primary standard. They are not attractive for ordinary use, as they involve the preparation of constant boiling sulphuric acid. This boils at 330° C at 1 atmosphere, and requires the use of boiling tubes or rods (SCHOLES[11]) to minimize bumping. As the impurities (other than water) in AnalaR concentrated sulphuric acid total 0.5 parts in 10,000, which is much smaller than the coefficient of variation of calibration of a burette or pipette, KUNZLER's methods would seem to add unnecessary complications for all but the most precise work, and AnalaR sulphuric acid (S.G. 1.84) was used as the starting material for this study.

On the prepared sulphuric acid solutions, specific gravities were determined by means of a specific gravity bottle at 20° C/20° C, temperature being controlled to ± 0.1° C. Sulphuric acid was determined gravimetrically as $BaSO_4$. The compositions calculated from equation (1), together with those found, are given in Table II, where each gravimetric result is the mean of five determinations.

TABLE II

ANALYSIS OF STOCK SULPHURIC ACID SOLUTIONS

	S.G. 20° C/20° C in air	% w/w in air calc.	Found % w/w	Found Standard Error	Diff. from calc. %
A	1.2515	33.665	33.659	± 0.0393	— 0.006
B	1.2780	36.792	36.778	0.0442	— 0.014
C	1.2828	37.352	37.346	0.0252	— 0.006
D	1.2944	38.692	38.690	0.0449	— 0.002
			Mean	± 0.0405	

Solutions A, B and D were analysed soon after preparation, but the gravimetric results for Solution C were not obtained until six months after preparation, the solution meanwhile being used for the hygroscopicity and storage tests described below.

The figures are satisfactory. In no case does the difference between the calculated figure and that found exceed the standard error of the gravimetric method, while the mean standard deviation of the latter is ± 0.09049, to be compared with PICKERING's ± 0.09043.

Hygroscopicity

Solution C of Table II (prepared by mixing 720 ml of concentrated sulphuric acid with 2 litres of water) was tested for absorption of moisture, by leaving weighed quantities, near those required for 1 litre of decinormal and 1 litre of normal sulphuric acid respectively, in various containers on a balance-pan for twenty minutes, and measuring the increase in weight during that period. Results are given in Table III, from which it is seen that the increase in weight was negligible, even in open beakers, so that no special precautions are required during weighing out.

TABLE III

HYGROSCOPICITY OF 37.352% SULPHURIC ACID

Weight of acid g	Conditions	Increase in wt. in 20 minutes mg	Increase in wt. in 20 minutes parts per 10,000
14.1	Open 100 ml conical flask	0.7	0.5
14.1	Open 100 ml beaker	1.6	1.1
14.1	100 ml beaker covered by watchglass	0.8	0.6
128.0	Open 250 ml conical flask	0.9	0.07
128.0	Open 250 ml beaker	2.2	0.17
128.0	250 ml beaker covered by watchglass	0.9	0.07

Storage

The remainder of Solution C (approximately 2 litres) was stored on the laboratory shelf, in a screw-capped glass Winchester, the cap being fitted with a rubber washer. At intervals averaging 10 days, over a period of 6 months, portions of 102 ml (approximately that required for 1 litre of $1N$ H_2SO_4) were poured into a cylinder and rejected, the mouth of the Winchester being immediately wiped with a dry filter-paper and the screw-cap replaced and tightened, after each withdrawal. The final 200 ml portion was examined for specific gravity and percentage of sulphuric acid.

The specific gravity at 20° C/20° C was 1.2831, an increase of 0.0003 in six months. This is probably due to extraction of material from the glass of the Winchester, and would be accounted for by about 0.04% of sodium silicate. As seen in Table II, the percentage of sulphuric acid found was in satisfactory agreement with that calculated six months previously from the specific gravity then found.

Recommended procedure for the preparation of standard solution of sulphuric acid

Pour 360 ml of concentrated sulphuric acid (S.G. 1.84) of analytical reagent purity into 1 litre of distilled water slowly with constant stirring. Cool, transfer to a suitably stoppered bottle. Determine specific gravity at 20° C/20° C, and from equation (1) calculate the percentage by weight in air. By means of equation (2) calculate the weight of this stock standard acid required to produce the required volume of standard acid of the required normality.

A single specific gravity determination is adequate for ordinary work, as the standard deviation of five measurements by specific gravity bottle on the same solution was found to be ± 0.000036, which corresponds to an error of the order of 1 part in 10,000. The temperature should be closely controlled as, according to DOMKE's results, the mean temperature correction between 32% and 39% of sulphuric acid is 0.00074 per degree centigrade, so that an error of 0.1° C would lead to an error of the order of 0.009% in the concentration or 2 parts per 10,000. Five-figure logarithms are used in equation (1) and the percentages rounded off to the third decimal place.

CONCLUSIONS

1. The percentage composition by weight of sulphuric acid solutions between 32% and 39% can be accurately computed from specific gravity determinations.
2. Such solutions can be weighed in open vessels without precautions against absorption of moisture. They can be kept in suitably capped bottles under ordinary conditions of use for at least six months.
3. The absence of hygroscopicity renders them superior to the 70% acid used

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by the A.O.A.C. for the preparation of standard solutions of sulphuric acid by direct weighing.

SUMMARY

The strength of solutions of pure sulphuric acid between 32% and 39% by weight can be accurately calculated from the specific gravity at 20° C/20° C by means of a simple equation. Such solutions can be kept for at least six months, are practically non-hygroscopic, and are suitable for the preparation of standard solutions of sulphuric acid by direct weighing.

RÉSUMÉ

La force des solutions d'acide sulfurique de 32 à 39% (en poids) peut être calculée avec précision au moyen d'une simple équation à partir de leur poids spécifique à 20° C/20° C. Ces solutions peuvent être conservées au moins six mois; pratiquement, elles ne sont pas hygroscopiques; elles conviennent pour la préparation de solutions étalon d'acide sulfurique par pesée directe.

ZUSAMMENFASSUNG

Die Stärke der Schwefelsäure zwischen 32 und 39% (in Gewicht) kann präzis berechnet werden mit Hilfe einer einfachen Gleichung auf Grund des spezifischen Gewichtes bei 20° C/20° C. Diese Lösungen können mindestens sechs Monate aufbewahrt werden; sie sind praktisch nicht hygroskopisch. Sie eignen sich für die Herstellung von Schwefelsäure — Standardlösungen durch direktes Wägen.

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CERATE OXIDIMETRY

II. OXIDATION OF MALEIC, FUMARIC, BENZOIC, SALICYLIC AND PHTHALIC ACIDS

by

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In an earlier publication[1] from these laboratories, it has been demonstrated that formic, glycolic, malic, malonic and tartaric acids can be oxidized completely to carbon dioxide and water by ceric sulphate in the presence of sulphuric acid.

WILLARD AND YOUNG[2] studied the oxidation of various other organic acids also. They found that acetic and succinic acids are not oxidized at all by boiling ceric sulphate solutions, maleic and fumaric acids consume only slight amounts of the reagent, while benzoic, salicylic and phthalic acids are oxidized to an appreciable extent by ceric sulphate at 90-100° C, but the oxidation of the last three acids also was variable. Accordingly the method could not be employed for their quantitative estimation. In view of the success achieved in the complete oxidation of acids like formic, glycolic, malic, malonic and tartaric acids, it was considered of interest to make a careful study of the oxidizability of the other acids also. It was confirmed that acetic and succinic acids are not affected by ceric sulphate even on boiling in the presence of higher concentrations of sulphuric acid. However, it has been possible to oxidize the other acids completely to carbon dioxide and water by ceric sulphate in the presence of sulphuric acid. Table I summarizes the results obtained.

TABLE I

Name of the acid	Equivalents of O_2 reqd. if oxidized completely to CO_2 and H_2O	Equivalents of O_2 actually consumed per mole of the acid
Maleic	12.00	11.98
Fumaric	12.00	11.93
Benzoic	30.00	29.92
Phthalic	30.00	29.98
Salicylic	28.00	28.01

EXPERIMENTAL

Materials. The ceric sulphate employed was a Schuchardt product and was used without further purification. Standardization of ceric sulphate solution was performed as described in an earlier publication[1].

Maleic acid

LANGE AND KLINE[3] stated that maleic and fumaric acids could be titrated with potassium permanganate in hot acid solution and assumed that the following reaction occurred:

$$H_2C_4H_2O_4 + 5\ O = 3CO_2 + HCOOH + H_2O$$

According to them, the method was not suitable for quantitative work. WILLARD AND YOUNG[2] expected that both maleic and fumaric acids should easily be oxidized by ceric sulphate in hot acid solution. Their experimental results, however, showed that a very small amount (less than 2 ml) of 0.1N ceric sulphate was consumed by 62 mg of either acid. They ignored this small oxidation and reported in the summary of their results that these acids are not oxidized by ceric sulphate. On repeating their work, we found that maleic acid is oxidized although the rate of oxidation is very slow. However, by increasing the concentration of sulphuric acid in the reaction mixture, it has been possible to oxidize maleic acid completely to carbon dioxide and water.

A Kahlbaum sample of the acid was recrystallized from hot acetone and the first crop of crystals was employed to prepare a standard solution. This was again standardized by titrating against $N/20$ caustic soda solution and the sample showed a percentage purity of 99.87%.

A measured volume of the maleic acid solution was added to a cooled mixture of ceric sulphate (excess) solution and concentrated sulphuric acid. The mixed solution was now refluxed in a boiling water bath and, afterwards, diluted to about 200 ml before titrating the excess ceric sulphate. The results obtained are tabulated in Table II.

TABLE II

Maleic acid soln ml	0.1115N $Ce(SO_4)_2$ ml	Conc. H_2SO_4 ml	Time of refluxing min	$Ce(SO_4)_2$ consumed by maleic acid ml	Maleic acid found g	Maleic acid present g
2.0	10	5	60	4.50	0.00485	0.00587
1.0	10	10	60	2.70	0.00292	0.00293
1.0	10	10	90	2.70	0.00292	0.00293
2.0	10	10	45	4.37	0.00471	0.00587
2.0	10	10	60	5.42	0.00585	0.00587
2.0	10	10	120	5.42	0.00585	0.00587
5.0	20	20	60	13.60	0.01466	0.01467
10.0	40	40	60	27.13	0.02926	0.02934

References p. 511.

Fumaric acid

WILLARD AND YOUNG[2] found that the behaviour of fumaric acid towards ceric sulphate was exactly similar to that of maleic acid. On treating fumaric acid with ceric sulphate in the presence of concentrated sulphuric acid, it has been found that this acid can also be oxidized completely to carbon dioxide and water, although the time required for complete oxidation is much longer than in the case of maleic acid.

TABLE III

Fumaric acid soln ml	0.1115N $Ce(SO_4)_2$ ml	Conc. H_2SO_4 ml	Time of refluxing min	$Ce(SO_4)_2$ consumed by fumaric acid ml	Fumaric acid found g	Fumaric acid present g
2.0	10	10	60	4.20	0.00453	0.00853
2.0	10	10	120	7.14	0.00771	0.00853
2.0	10	10	150	7.91	0.00853	0.00853
2.0	10	10	180	7.91	0.00853	0.00853
5.0	30	30	150	19.77	0.02132	0.02134
5.0	30	30	180	19.79	0.02135	0.02134

Benzoic acid

Benzoic acid is very resistant to oxidizing agents; even alkaline permanganate is not able to oxidize it[4]. WILLAND AND YOUNG[2] attempted its oxidation with ceric sulphate and found that it was oxidized to a considerable but indefinite extent. However, it has been possible to oxidize it completely to carbon dioxide and water by increasing the concentration of sulphuric acid.

Benzoic acid (Schuchardt) was crystallized first from alcohol and subsequently from ether. The first crop of crystals was used to prepare a standard solution in dilute caustic soda solution. The oxidation of this solution was studied in the same manner as described for maleic acid. The results obtained are tabulated in Table IV.

TABLE IV

Benzoic acid soln ml	0.1025N $Ce(SO_4)_2$ ml	Conc. H_2SO_4 ml	Time of refluxing min	$Ce(SO_4)_2$ consumed by benzoic acid ml	Benzoic acid found g	Benzoic acid present g
2.0	10	24	60	3.75	0.00156	0.00192
2.0	10	24	120	4.58	0.00191	0.00192
2.0	10	24	150	4.60	0.00192	0.00192
2.0	10	28	120	4.60	0.00192	0.00192
2.0	10	12	60	2.98	0.00124	0.00192
2.0	10	12	120	3.81	0.00169	0.00192
2.0	10	12	180	4.4	0.00183	0.00192
2.0	10	12	240	4.59	0.00191	0.00192
2.0	10	12	270	4.58	0.00191	0.00192
5.0	15	20	240	11.49	0.00575	0.00576

Phthalic acid

Willard and Young[2] found that phthalic acid was oxidized to a slight extent only by ceric sulphate.

A solution of phthalic acid (Kahlbaum) was prepared and standardized as acid by titrating against *N*/20 sodium hydroxide solution. Measured volumes of this solution were treated with ceric sulphate as described for maleic acid and the results obtained are given in Table V.

TABLE V

Phthalic acid soln ml	0.1115*N* $Ce(SO_4)_2$ ml	Conc. H_2SO_4 ml	Time of refluxing min	$Ce(SO_4)_2$ consumed by phthalic acid ml	Phthalic acid found g	Phthalic acid present g
2.0	10	12	60	2.20	0.00137	0.00203
2.0	10	12	120	3.05	0.00190	0.00203
2.0	10	12	180	3.25	0.00202	0.00203
2.0	10	12	240	3.25	0.00202	0.00203
5.0	20	25	180	8.15	0.00507	0.00506
5.0	15	20	180	8.15	0.00507	0.00506

Salicylic acid

Willard and Young oxidized salicylic acid by ceric sulphate and stated that, "oxidation of salicylic acid is quite extensive, but not constant".

Recrystallized sodium salicylate was used to prepare a standard solution by weight and known volumes of this solution were treated with ceric sulphate as before. The results are given in Table VI.

TABLE VI

Salicylic acid soln ml	0.1115*N* $Ce(SO_4)_2$ ml	Conc. H_2SO_4 ml	Time of refluxing min	$Ce(SO_4)_2$ consumed by salicylic acid ml	Salicylic acid found g	Salicylic acid present g
2.0	5	7	60	2.40	0.00132	0.00151
2.0	5	7	120	2.64	0.00145	0.00151
2.0	5	7	150	2.73	0.00150	0.00151
2.0	10	12	180	2.73	0.00150	0.00151
5.0	15	20	150	6.85	0.00377	0.00376
5.0	10	15	150	6.83	0.00375	0.00376

SUMMARY

1. It has been shown that maleic, fumaric, benzoic, phthalic and salicylic acids can be oxidized completely to carbon dioxide and water by ceric sulphate in the presence of concentrated sulphuric acid.

2. These acids can be estimated quantitatively by the use of ceric sulphate.

3. Acetic and succinic acids are not oxidized by ceric sulphate even in the presence of high concentrations of sulphuric acid.

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RÉSUMÉ

1. Il est démontré que les acides maléique, fumarique, benzoïque, phtalique et salicylique peuvent être oxydés quantitativement en anhydride carbonique et eau par le sulfate de cérium(IV), en présence d'acide sulfurique concentré.

2. Ces acides peuvent être dosés ainsi par le sulfate de cérium(IV).

3. Les acides acétique et succinique ne sont pas oxydés par le sulfate de cérium (IV) même en présence d'acide sulfurique très concentré.

ZUSAMMENFASSUNG

1. Es wird gezeigt, dass die Malein-, Fumarin-, Benzol-, Phtal- und Salicylsäure quantitativ in Kohlendioxyd und Wasser oxydiert werden können durch Cerium (IV) sulfat in Gegenwart von konzentrierter Schwefelsäure.

2. So können diese Säuren durch Cerium(IV) sulfat bestimmt werden.

3. Die Essig- und Bernsteinsäure werden durch Cerium(IV) sulfat nicht oxydiert, selbst bei Gegenwart von sehr konzentrierter Schwefelsäure.

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OXIDATION WITH ALKALINE PERMANGANATE USING FORMIC ACID FOR THE BACK-TITRATION

I. DETERMINATION OF QUADRIVALENT TELLURIUM AND THE REDOX POTENTIAL OF THE TeO_4^{-2}/TeO_3^{-2} SYSTEM

by

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In a previous investigation, one of us[1], studied the oxidation of quadrivalent tellurium by permanganate in weakly alkaline solutions ($\sim$ 0.08*N* NaOH). Under these conditions reduction of MnO_4^- proceeds quantitatively to MnO_2. This is in conformity with the magnitude of the equilibrium constant of the reaction K and its degree of completion α which amount to $7.32 \cdot 10^{-21}$ and $1.49 \cdot 10^{-4}$ as calculated from the redox potential values of the systems involved in the reaction:

$$3\ Te^{+4} + 2\ Mn^{+7} \rightarrow 3\ Te^{+6} + 2\ Mn^{+4}$$

viz. that of the TeO_4^{-2}/TeO_3^{-2} system = 0.4[2] volt and of the MnO_4^-/MnO_2 couple = 0.588[3] volt together with the number of faradays necessary to complete the reaction (*i.e.* 6) and the respective valency changes of both systems (*i.e.* 2 and 3).

However, in trying to calculate the equilibrium constant and the degree of completion of the reaction taking place in strong alkaline solutions, in which reduction of MnO_4^- yields MnO_4^{-2}:

$$Te^{+4} + 2\ Mn^{+7} \rightarrow Te^{+6} + 2\ Mn^{+6}$$

and upon which some recommended procedure is based[13], one comes to the conclusion that contrary to expectation quantitative results are not possible. Thus by using the E_0 of the MnO_4^-/MnO_4^{-2} system (0.564 volt[2]) together with the above value for the TeO_4^{-2}/TeO_3^{-2} couple, the number of faradays to complete the reaction (*i.e.* 2) and the respective valency changes of both pairs of ions (*i.e.* 1 and 2), K and α amount to $2.76 \cdot 10^{-6}$ and $1.04 \cdot 10^{-2}$.

In this investigation the direct oxidation of quadrivalent tellurium with permanganate was studied under a variety of conditions, including, the concentration of the reactants and the alkalinity of the reaction medium and the evaluation of the redox potential of the TeO_4^{-2}/TeO_3^{-2} system which in view of the authors is much less than 0.4 volt, as given by LATIMER[2]. It was also aimed to devise a procedure depending upon the oxidation of Te^{+4} with MnO_4^- in strong alkaline solution and back titrating excess oxidant with formic acid[4].

EXPERIMENTAL

Preparation and standardisation of solutions

Solutions of quadrivalent tellurium. These were prepared by dissolving potassium tellurite grade Scherring Kahlbaum in hot water containing 0.05*N* NaOH, which is taken into consideration when calculating the alkalinity of the solution to be titrated. The tellurium content of these solutions was determined by two methods, which gave concordant results[1,5].

Solutions of potassium permanganate. These were prepared according to STAMM's method[6] and standardized with sodium oxalate grade AnalaR[7] and with formic acid[4].

Solutions of lower concentrations were prepared by the appropriate dilution of the more concentrated tellurite or permanganate solutions with twice distilled water.

Working procedure

The reactions under consideration were studied potentiometrically using for the titration processes a device similar to that described previously[8].

a) In carrying out the titrations the appropriate volume of the tellurite solution was mixed with the requisite quantity of 5*N* NaOH to bring the alkalinity to 0.1 — 4*N*. The solutions were then titrated with permanganate in the presence or absence of telluric acid.

b) In titrating permanganate with tellurite, the former solution was made 0.5 to 3*N* with respect to NaOH, and then titrated with tellurite in the presence or absence of Ba^{+2} ions or telluric acid.

c) In the indirect determination of Te^{+4}, the tellurite solution is mixed with excess $KMnO_4$ in the presence of 1.5 — 2*N* NaOH and the excess of the oxidant is then titrated with formic acid solution[4].

RESULTS

Oxidation of quadrivalent tellurium with potassium permanganate

The results obtained by oxidizing quadrivalent tellurium solutions of normalities varying from $8.896 \cdot 10^{-2}$ to $1.834 \cdot 10^{-5} N$ — in the absence of telluric acid — with $2.194 \cdot 10^{-2}$ to $4.192 \cdot 10^{-5} M$ potassium permanganate solutions, in the presence of 0.1–4*N* NaOH are shown in Table I. These indicate that in the case of the more concentrated solutions (∿ 0.02-0.09*N*), reduction of potassium permanganate proceeds almost quantitatively to MnO_2 irrespective of the alkali concentration applied. The maximum error amounting to 0.5% is obtained in the presence of 4*N* NaOH. The end-points are attended with sharp inflections amounting to 120-190 mv per 0.1 ml of permanganate solution depending on the Te^{+4} concentration. The reaction takes place rapidly, needing for the attainment of equilibrium only 1-2 min at the beginning of the titration, and 3-5 min near the end-point.

By decreasing the concentration of both reactants and keeping the alkali concentration at $3.5N$, reduction of MnO_4^- ions to the manganate state becomes considerable, such that at a concentration of $Te^{+4} = 4.585 \cdot 10^{-4}$ to $1.834 \cdot 10^{-5}N$ and of $MnO_4^- = 2.096 \cdot 10^{-3}$ to $4.192 \cdot 10^{-5}M$ reduction proceeds almost quantitatively to manganate. The optimum alkali concentration suitable for complete

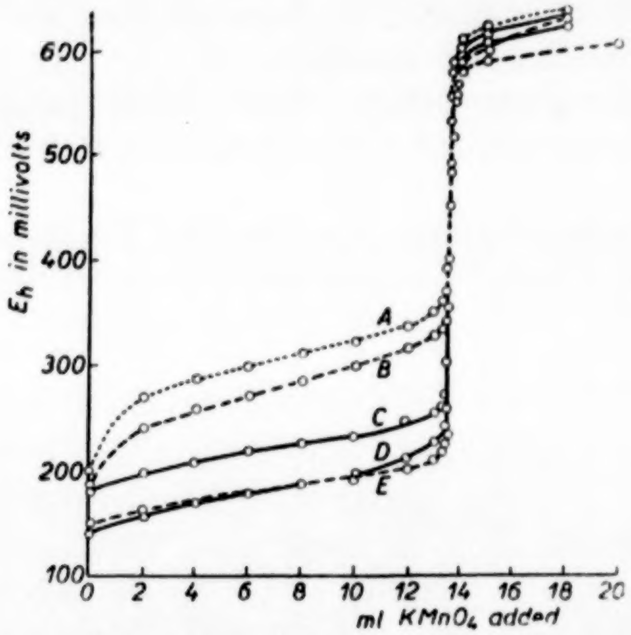

Fig. 1. Titration of 10 ml $8.896 \cdot 10^{-2}N$ Te^{+4} with $2.194 \cdot 10^{-2}M$ $KMnO_4$
A) $0.1N$ NaOH B) $1N$ NaOH C) $2N$ NaOH
D) $3N$ NaOH E) $4N$ NaOH

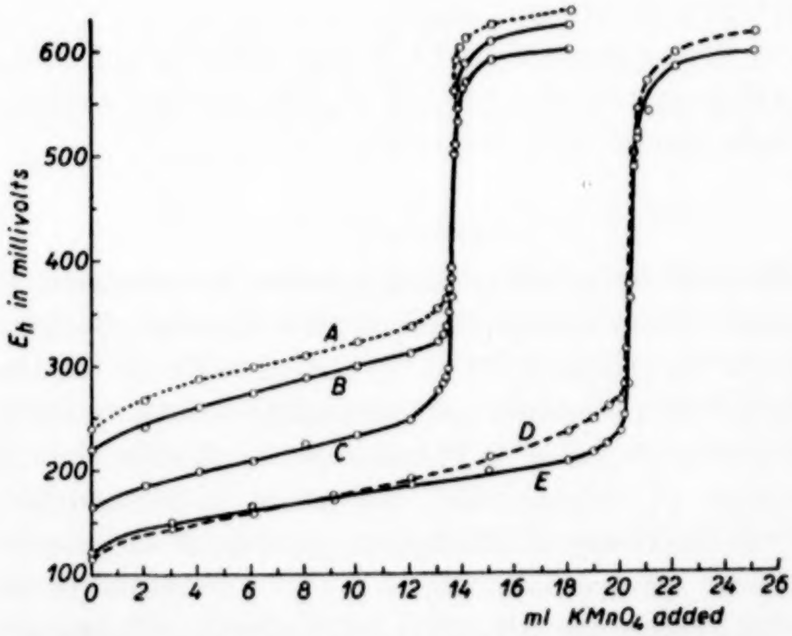

Fig. 2. Titration of $2.224 \cdot 10^{-2}N$ Te^{+4} with $5.485 \cdot 10^{-3}M$ $KMnO_4$
A) 10 ml Te^{+4} in $0.1N$ NaOH B) 10 ml Te^{+4} in $1N$ NaOH
C) 10 ml Te^{+4} in $2N$ NaOH D) 15 ml Te^{+4} in $3N$ NaOH
E) 15 ml Te^{+4} in $4N$ NaOH

References p. 523.

reduction of MnO_4^- is 3–3.5*N* (see Table II). The inflections in the case of the more concentrated solutions ($Te^{+4} = 4.585 \cdot 10^{-4} N$) are more or less distinct amounting to 50-70 mv per 0.1 ml of titrant (*cf.* Fig. 3), but decrease by diluting the reacting solutions so that when the concentration of Te^{+4} is $1.834 \cdot 10^{-6} N$ and that of $KMnO_4$ is $4.192 \cdot 10^{-6} M$ no inflection is observed. This is also the case when the alkali concentration is made 4*N*, in which case the pink permanganate does not persist after the end-point as a result of autodecomposition[5,9,10].

Here, again, the equilibria are attained rapidly needing 1-2 min at the beginning of the titration and ∿ 3 min at the end-point.

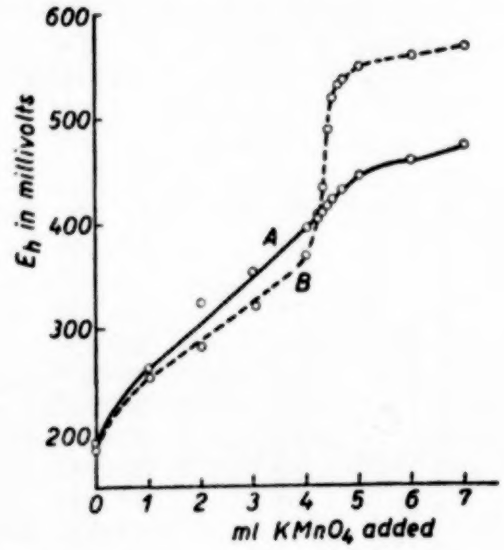

Fig. 3. Titration of 10 ml $1.834 \cdot 10^{-4} N$ Te^{+4} with $4.192 \cdot 10^{-4} M$ $KMnO_4$
A) In 4*N* NaOH B) In 3*N* NaOH

TABLE I

TITRATION OF Te^{+4} WITH $KMnO_4$ TO GIVE MnO_2

Alkali concn.	Max inflecn. per 0.1 ml $KMnO_4$	Te present/l	Te found/l	Error %
10 ml $8.896 \cdot 10^{-2} N$ Te^{+4} titrated with $2.194 \cdot 10^{-2} M$ $KMnO_4$:				
0.1*N* NaOH	169 mv	5.6806 g	5.6803 g	—0.10
1*N* ,,	149 ,,	5.6806 ,,	5.6914 ,,	0.19
2*N* ,,	147 ,,	5.6806 ,,	5.6954 ,,	0.26
3*N* ,,	171 ,,	5.6806 ,,	5.7079 ,,	0.48
4*N* ,,	171 ,,	5.6806 ,,	5.7090 ,,	0.50
10 ml $2.224 \cdot 10^{-2} N$ Te^{+4} titrated with $5.485 \cdot 10^{-3} M$ $KMnO_4$				
0.1*N* NaOH	151 mv	1.4202 g	1.4212 g	0.11
1*N* ,,	116 ,,	1.4202 ,,	1.4233 ,,	0.22
2*N* ,,	137 ,,	1.4202 ,,	1.4229 ,,	0.19
3*N* ,,	125 ,,	1.4202 ,,	1.4247 ,,	0.32
4*N* ,,	126 ,,	1.4202 ,,	1.4258 ,,	0.38

Oxidation of Te^{+4} with $KMnO_4$ was also carried out in 0.1N NaOH in the presence of telluric acid. In this case, manganese dioxide did not separate out and the solution assumed a rose colour. The inflection at the end-points is very sharp and the reaction rapid, but slows near the end-point needing 5 min for the attainment of equilibrium, which time decreases only to 4 min in the presence of NaCl. The results are also as accurate as in absence of telluric acid (*cf.* Table III).

TABLE II

TITRATION OF Te^{+4} WITH $KMnO_4$ TO GIVE MnO_4^{-2}

Normality of Te^{+4}	Normality of $KMnO_4$	Alkali concn.	Max inflecn. per 0.1 ml $KMnO_4$	Te present/l	Te found/l	Error %
$1.83 \cdot 10^{-3} N$	$2.096 \cdot 10^{-3} M$	3.5 N	66 mv	117.112 mg	65.198 mg	—35.79
$9.17 \cdot 10^{-4} N$	$2.74 \cdot 10^{-3} M$	3.5 N	48 ,,	58.556 ,,	54.949 ,,	—6.16
$4.585 \cdot 10^{-4} N$	$2.096 \cdot 10^{-3} M$	2 N	70 ,,	29.278 ,,	26.628 ,,	—9.05
,,	,,	3 N	75 ,,	29.278 ,,	29.372 ,,	0.32
,,	,,	3.25N	79 ,,	29.278	29.331 ,,	0.18
,,	,,	3.5 N	59 ,,	29.278 ,,	29.331 ,,	0.18
,,	,,	3.75N	54 ,,	29.278	29.372 ,,	0.32
$1.834 \cdot 10^{-4} N$	$4.192 \cdot 10^{-4} M$	2 N	50 ,,	11.711 mg	11.581 ,,	—1.11
,,	,,	3 N	56 ,,	11.711 ,,	11.884 ,,	0.23
,,	,,	3.5 N	67 ,,	11.711 ,,	11.724 ,,	0.11
$1.834 \cdot 10^{-5} N$	$4.192 \cdot 10^{-5} M$	3.25N	12 ,,	1.171 mg	1.174 ,,	0.26
,,	,,	3.25N	12 ,,	1.171 ,,	1.175 ,,	0.33

TABLE III

TITRATION OF Te^{+4} IN 0.1N NaOH WITH $KMnO_4$ IN PRESENCE OF TELLURIC ACID

Normality of Te^{+4}	Normality of $KMnO_4$	Max. inflecn.	Te present/l	Te found/l	Error %	Other conditions
$7.93 \cdot 10^{-2}$	$6.977 \cdot 10^{-2}$	225 mv	5.0637 g	5.0679 g	0.26	Pt electrode
,,	,,	230 ,,	5.0637 ,,	5.0769 ,,	0.26	Pt, NaCl
,,	,,	53 ,,	5.0637 ,,	5.0419 ,,	—0.43	Cr electrode
$7.93 \cdot 10^{-3}$	$6.977 \cdot 10^{-3}$	142 ,,	0.5064 ,,	0.5077 ,,	0.26	Pt, NaCl
$7.93 \cdot 10^{-4}$	$6.977 \cdot 10^{-4}$	76 ,,	50.64 mg	50.81 mg	0.34	Pt, NaCl
$7.93 \cdot 10^{-5}$	$6.977 \cdot 10^{-5}$	27 ,,	5.064 ,,	5.081 ,,	0.34	Pt, NaCl

Reduction of potassium permanganate with quadrivalent tellurium

(a) In the titration of 0.1260N $KMnO_4$ with 0.0463-0.0917N Te^{+4} solutions at different alkali concentrations and in the absence of Ba^{+2} ions no inflection is observed corresponding to the reduction of MnO_4^- to MnO_4^{-2} (*cf.* Curves A, B and C Fig. 4) although the reaction yields initially a mixture of MnO_4^{-2} and MnO_2. In the

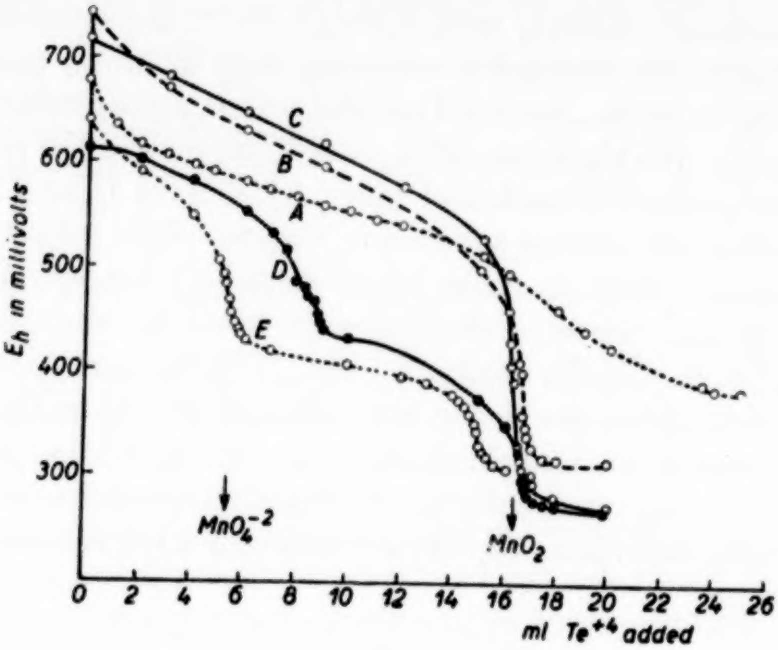

Fig. 4.

A) Titration of 25 ml $2.74\cdot10^{-2}M$ $KMnO_4$ in $0.5N$ NaOH with $9.17\cdot10^{-2}N$ Te^{+4}
B) Titration of 10 ml $2.52\cdot10^{-2}M$ $KMnO_4$ in $1N$ NaOH with $4.63\cdot10^{-2}N$ Te^{+4}
C) Titration of 10 ml $2.52\cdot10^{-2}M$ $KMnO_4$ in $3N$ NaOH with $4.63\cdot10^{-2}N$ Te^{+4}
D) Titration of 10 ml $2.498\cdot10^{-3}M$ $KMnO_4$ in $2N$ NaOH with $4.5\cdot10^{-3}N$ Te^{+4}
E) Titration of 2 ml $2.498\cdot10^{-3}M$ $KMnO_4$ in $1.5N$ NaOH with $9\cdot10^{-4}N$ Te^{+4}

vicinity of the end-point corresponding to the formation of MnO_2, and before that point is reached (by ∿ 2%), the solutions assume an intense reddish colour. The sharp inflection corresponding to the end-point of the reaction (amounting to ∿ 50 mv) occurs, however, after the end-point corresponding to MnO_2 by ∿ 2%, owing perhaps to partial reduction of MnO_4^- to Mn^{+3} as the permanganate concentration decreases. This is favoured by the fact that by increasing the alkali concentration the error due to the formation of Mn^{+3} decreases (Table IV A).

TABLE IV A

TITRATION OF $KMnO_4$ WITH Te^{+4} IN THE ABSENCE OF Ba^{+2} IONS OR TELLURIC ACID
10 ml $0.1260N$ $KMnO_4$ titrated with $0.0463N$ Te^{+4}

Alkali concn.	Max inflection per 0.1 ml Te^{+4}	End-point Mn^{+4} calculated	End-point found	Error %
$1N$	66 mv	16.32 ml	16.68 ml	2.22
$1.5N$	40 ,,	16.32 ,,	16.67 ,,	2.14
$2N$	65 ,,	16.32 ,,	16.57 ,,	1.50
$2.5N$	51 ,,	16.32 ,,	16.53 ,,	1.29
$3N$	63 ,,	16.32	16.47 ,,	0.90

References p. 523.

On titrating 0.01249N $KMnO_4$ with 0.0045N Te^{+4}, the error due to trivalent manganese decreases; the end-point corresponding to MnO_2 occurs only 0.7% late. Contrary to the more concentrated solutions used, a poor inflection amounting to 8-13 mv appears in the titration curve 50-60% later than the manganate state due apparently to partial formation of MnO_2 (*cf.* Curves D and E Fig. 4).

By further diluting the tellurite solution to $1.13 \cdot 10^{-3}N$ the inflection corresponding to the manganate state becomes more apparent amounting under these conditions to $\sim$ 20 mv, whereas that corresponding to MnO_2 becomes poorer. As may be seen from the results shown in Table IV B the end-point corresponding to manganate in this latter case lies in the region of the theoretical value. In all diluted solutions except the tenfold diluted one, the end-point corresponding to MnO_2 occurs early, owing apparently to the autodecomposition of permanganate.

The above reaction takes place rapidly needing only a few minutes for the attainment of equilibrium.

TABLE IV B

0.01249N $KMnO_4$ TITRATED WITH Te^{+4}

Theoretical end-point Mn^{+6} = 5.56 ml, Mn^{+4} = 16.68 ml

Vol of $KMnO_4$	Te^{+4} concn.	Alkali conc.	Max inflection		End-point		Error %	
			Mn^{+6}	Mn^{+4}	Mn^{+6}	Mn^{+4}	Mn^{+6}	Mn^{+4}
10 ml	0.0045N	2 N	13 mv	21 mv	8.8 ml	16.8	58.3	0.72
10 ,,	0.0045N	2.5N	8 ,,	17 ,,	8.5 ,,	16.8	52.9	0.72
5 ,,	0.00225N	2 N	19 ,,	17 ,,	7.2 ,,	16.1	29l5	—3.47
5 ,,	0.00225N	2.5N	10 ,,	17 ,,	7.2 ,,	15.2	29.5	—8.87
2.5 ml	0.00113N	2 N	19 ,,	17 ,,	5.7 ,,	16.5	2.52	—0.90
2.5 ,,	0.00113N	2.5N	21 ,,	17 ,,	5.6 ,,	—	0.72	—

(b) Better results are obtained when the titrations are performed in the presence of telluric acid. This latter reagent dissolves any manganese dioxide[11] formed thus preventing its catalytic effect on the decomposition of $KMnO_4$. It also prevents, by virtue of its complexing action on quadrivalent manganese, the reduction of permanganate to trivalent manganese. The solution assumes a rose colour different from that obtained in the absence of telluric acid. The reaction occurring under these conditions takes place rapidly at the beginning but slows near the end-point, needing 8-12 min for the attainment of equilibrium. In the case of the more concentrated solutions used (0.0405N), — as in the absence of telluric acid — a single inflection corresponding to the manganite state is observed. However, on using Te^{+4} solutions as dilute as 4.05 to $8.1 \cdot 10^{-3}N$ another inflection (amounting to 28-23 mv) corresponding to the manganate state is observed but occurs 44 and 21% late with both solutions respectively.

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TABLE V

TITRATION OF $KMnO_4$ IN PRESENCE OF TELLURIC ACID WITH Te^{+4}

Alkali concn.	Normality of $KMnO_4$	Normality of Te^{+4}	Max. inflection	Te equiv. to $KMnO_4$ to yield MnO_2	Te consumed in reaction	Error %
0.5*N*	0.1163	$4.05 \cdot 10^{-2}$	75 mv	44.559	44.702	0.32
1.5*N*	0.1163	$4.05 \cdot 10^{-2}$	104 ,,	44.559	44.666	0.24
2.5*N*	0.1163	$4.05 \cdot 10^{-2}$	66 ,,	44.559	44.630	0.16
1.5*N*	$2.326 \cdot 10^{-2}$	$8.1 \cdot 10^{-3}$	30 ,,	8.912	8.926	0.16
1.5*N*	$2.326 \cdot 10^{-2}$	$4.05 \cdot 10^{-3}$	8 ,,	4.456	4.430	0.58

(c) In trying to check the reduction of permanganate at the manganate state by adding Ba^{+2} ions, the results obtained are attended with considerable errors. The end-points are attained late, due in part to precipitation of the $BaTeO_3$ which escapes oxidation and in part to the partial reduction of $KMnO_4$ to MnO_2 (*cf.* Table VI). The errors decrease by decreasing the concentration of the reactants and the amount of Ba^{+2} ions added. A large quantity of Ba^{+2} ions leads to an early end-point due possibly to their catalytic effect on the decomposition of permanganate[12].

TABLE VI

TITRATION OF $KMnO_4$ WITH Te^{+4} IN PRESENCE OF Ba^{+2} IONS

Vol. & Normality of $KMnO_4$	Alkali concn.	Te^{+4} concn.	ml 5% $Ba(NO_3)_2$	Max infl. per 0.1 ml Te^{+4}	Error %
10 ml 0.1260*N*	0.5*N*	0.0463	5 ml	76 mv	58.09
10 ml 0.1260*N*	1 *N*	0.0463	5 ,,	60 ,,	53.12
10 ml 0.01249*N*	1 *N*	0.0018	2 ,,	30 ,,	18.87
5 ml 0.01249*N*	1 *N*	0.0009	2 ,,	100 ,,	4.47
2.5 ml 0.01249*N*	1 *N*	0.00045	2 ,,	87 ,,	1.40
2.5 ml 0.01249*N*	1 *N*	0.00045	2 ,,	131 ,,	1.59

Oxidation of Te^{+4} with $KMnO_4$ and back-titrating excess with formic acid

MOSER AND MIKSCH[13] suggested, for the determination of quadrivalent tellurium, a method depending upon oxidation of the latter with excess $KMnO_4$ in strong alkaline solution. Oxalic acid is then added to the mixture and the excess of this latter reagent determined with permanganate after making the solution acid.

However, as may be visualized from the above results reduction of $KMnO_4$ with Te^{+4} leads primarily to the production of manganate together with MnO_2, Since the process devised allows the reduction to proceed only to manganate, we used to add the tellurite solution to excess $KMnO_4$ dropwise in presence of 1.5-2*N* NaOH, while continuously stirring the permanganate. If the addition is made rapidly, reduction proceeds unavoidably, although partially to MnO_2, and this will lead to considerable errors. Since the equilibrium in this reaction is attained rapidly (as shown before) it is possible to titrate the excess of $KMnO_4$ a few minutes after the last drop of the tellurite solution has been added.

As may be seen from the data shown in Table VII good results could only be obtained if the permanganate present is more than double the amount equivalent to the tellurite added. Where a slight excess of $KMnO_4$ is present, the amount of tellurium obtained is low as a result of the partial reduction of $KMnO_4$ to MnO_2.

TABLE VII

Vol. & Normality of $KMnO_4$	Normality of formic acid	Vol. & Normality of Te^{+4}	Te mg	Te mg	Error %
25 ml 0.1163*N*	0.0245	10 ml 0.0425*N*	27.138	25.274	—6.87
25 ml 0.1163*N*	0.0999	5 ml 0.0425*N*	13.569	13.532	—0.27
25 ml 0.1163*N*	0.0999	2 ml 0.0425*N*	5.428	5.452	0.44
10 ml 0.1163*N*	0.0245	5 ml 0. 01*N*	3.193	3.184	—0.27
10 ml 0.1163*N*	0.0245	2 ml 0. 01*N*	1.277	1.281	0.35
10 ml 0.1163*N*	0.0245	5 ml 0. 001*N*	0.399	0.321	0.54

The formal redox potential of the TeO_4^{-2}/TeO_3^{-2} system

From the theoretical point of view it is not possible to give a value for the redox potential of the TeO_4^{-2}/TeO_3^{-2} system since thermal data on telluric acid H_2TO_4 and the ion TeO_4^{-2} give results which are in disagreement with chemical properties[2]. The $E_{0(OH)}$ value as evaluated from oxidation of tellurite with hypoiodite is 0.4 volt[2].

From the results obtained above it is clear that the reaction between dilute tellurite and permanganate proceeds quantitatively in strong alkaline solution to yield tellurate and manganate. This throws much doubt on the value 0.4 volt[2] which is considered to represent the redox potential of the TeO_4^{-2}/TeO_3^{-2} system and upon which the improbable value $1.04 \cdot 10^{-2}$ for the degree of completion of this reaction as obtained before (page 572) is based.

Recourse was therefore taken to evaluate the redox potential values E_f of this system at different alkali concentrations from the titration curves of tellurite with permanganate (Figs. 1, 2 and 3). The titrations were performed at a constant temperature amounting to 25°C ± 0.1. The E_f values were calculated by applying the relation:

$$E_h = E_0 + \frac{RT}{2F} \ln \frac{[Te^{+6}]}{[Te^{+4}]}$$

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and subsituting for E_f the symbol $E_{o,}$ since in these calculations no account is taken for the activity coefficients of the ions concerned. By calculating E_f at 3 different stages of neutralization *viz.* when 30, 50 and 70% of tellurite is oxidized to tellurate, the data listed in Table VIII are obtained.

By plotting the E_f values against the OH^- ion concentration, curves A and B, Fig. 5, are obtained. Curve A represents E_f values corresponding to the higher tellurite concentrations ($\sim$ 0.02 — 0.09N) which reduce permanganate completely to MnO_2 (see Table I) whereas curve B represents the values obtained with more dilute solutions ($1.83 \cdot 410^{-4} N$) and under conditions favouring reduction of $KMnO_4$ to manganate (see Table II).

From curve A it is apparent that E_f for the TeO_4^{-2}/TeO_3^{-2} couple decreases with rise of OH^- ion concentration between 0.1 and 2.7N NaOH, above which it assumes an approximately constant value. The E_f values are constant within the concentration limit of quadrivalent tellurium applied (*viz.* 0.02-0.09N), but tend to more positive values as the concentration decreases further to $1.834 \cdot 10^{-4} N$ (*cf.* curve B, Fig. 5). This is in harmony with the fact that concentrated tellurite solutions reduce permanganate to MnO_2 but the dilute solutions only to manganate when the alkali concentration is kept the same in both cases at $\sim 3N$. $E_{f(OH)}$ the formal redox potential value at unit OH^- ion concentration as obtained by interpolation in curve A, Fig. 3, amounts to $\sim$ 0.26 volt which is less positive than the $E_{f(OH)}$ value hitherto known[2].

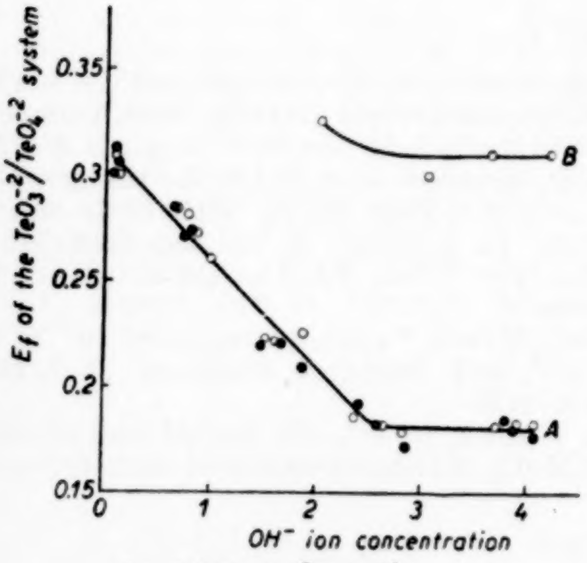

Fig. 5.

By calculating the degree of completion of the reaction which takes place at high alkali concentrations and leads to the reduction of permanganate to manganate, using E_f values amounting to 0.30-0.31 volt at 3-3.6N NaOH together with the E_o of the MnO_4^-/MnO_4^{-2} system *viz.* 0.564 volt[3], the degree of completion of the reaction is found to amount to $1.04–2.46 \cdot 10^{-3}$ which is better than the improbable value $1.04 \cdot 10^{-2}$ obtained using 0.4 for $E_{o(OH)}$ of the TeO_4^{-2}/TeO_3^{-2} couple. The value $1.04–2.46 \cdot 10^{-3}$ indicates that the reaction between dilute solution of tellurite and permanganate can take place quantitatively as found experimentally, favouring thus a lower value for $E_{o(OH)}$ of the TeO_4^{-2}/TeO_3^{-2} system.

p. 520, in Table VII, third column, lines 4, 5 and 6 should read 0.01N, 0.01N and 0.001N respectively.

p. 520, line 6 above formula, for page 572 read page 512.

TABLE VIII

E_f VALUES OF THE TeO_4^{-2}/TeO_3^{-2} COUPLE FROM TITRATION CURVES

Te^{+4} = 70 % Te^{+6} = 30 %		Te^{+4} = 50 % Te^{+6} = 50 %		Te^{+4} = 30 % Te^{+6} = 70 %	
Alkalinity	E_f in volt	Alkalinity	E_f in volt	Alkalinity	E_f in volt
		(A) Te^{+4} = $8.896 \cdot 10^{-2}N$			
0.11*N*	0.298	0.09*N*	0.305	0.08*N*	0.307
0.86*N*	0.273	0.74*N*	0.282	0.85*N*	0.283
1.85*N*	0.226	1.63*N*	0.221	1.47*N*	0.223
2.85*N*	0.179	2.60*N*	0.183	2.40*N*	0.186
4.07*N*	0.183	3.87*N*	0.183	3.70*N*	0.182
1 *N*	0.257	1 *N*	0.255	1 *N*	0.253
		(B) Te^{+4} = $2.22 \cdot 10^{-2}N$			
0.084*N*	0.299	0.07*N*	0.305	0.06*N*	0.209
0.83 *N*	0.274	0.72*N*	0.280	0.63*N*	0.285
1.83 *N*	0.209	1.62*N*	0.214	1.45*N*	0.219
2.84 *N*	0.171	2.59*N*	0.182	2.38*N*	0.191
4.06 *N*	0.176	3.87*N*	0.180	3.69*N*	0.184
1 *N*	0.256	1 *N*	0.258	1 *N*	0.251
		(C) Te^{+4} = $1.834 \cdot 10^{-4}N$			
		2*N*	0.325		
		3.02*N*	0.30		
		3.63*N*	0.31		
		4.19*N*	0.31		

SUMMARY

On oxidizing Te^{+4} of concentration varying from ∼ 0.02 — 0.09*N* with $KMnO_4$, reduction of $KMnO_4$ proceeds in 0.1-4*N* NaOH quantitatively to MnO_4. With a concentration of Te^{+4} — $4.585 \cdot 10^{-4}$ — $1.834 \cdot 10^{-5}$, of $KMnO_4$ = $2.096 \cdot 10^{-3}$ — $4.192\ 10^{-5}M$, and of NaOH = 3 — 3.5, reduction of $KMnO_4$ proceeds completely to manganate.

Reduction of $KMnO_4$ with Te^{+4} ($4.63 \cdot 10^{-2}N$) yields MnO_4 with little Mn^{+3}, without an inflection at the manganate state. In presence of telluric acid Mn^{+3} does not form and the reaction is quantitative. With Te^{+4} = $4.5\text{-}1.13 \cdot 10^{-3}$ an inflection corresponding to manganate occurs.

The formal redox potential E_f of the TeO_4^{-2}/TeO_3^{-2} system decreases with increasing alkali concentration from 0.1-2.7*N*, but becomes constant at higher alkalinities. E_f is constant at Te^{+4} = 0.09-0.02*N*.

Te^{+4} can be determined by mixing with $KMnO_4$ in 1.5-2*N* NaOH and stirring the mixture at room temperature. Excess $KMnO_4$ is then determined with formate.

RÉSUMÉ

Par oxydation de Te^{+4} (environ 0.02 à 0.09*N*) au moyen de permanganate de potassium, ce dernier se transforme quantitativement en MnO_2, en milieu NaOH 0.1 à 4*N*. Avec les concentrations suivantes: Te^{+4} $4.585 \cdot 10^{-4}$ à $1.834 \cdot 10^{-5}N$, $KMnO_4$ $2.096 \cdot 10^{-3}$ à $4.192 \cdot 10^{-5}M$ et NaOH 3 à 3.5*N*, on obtient une réduction quantitative du permanganate en manganate. La réduction de $KMnO_4$ par Te^{+4} ($4.63 \cdot 10^{-2}N$) conduit à MnO_2 accompagné d'un peu de Mn^{+3}, sans formation de

manganate. En présence d'acide tellurique, Mn^{+3} ne se forme pas et la réaction est quantitative. Avec Te^{+4} 4.5 à $1.13 \cdot 10^{-3}N$, on observe le passage en manganate. Le potentiel du système TeO$_4^{-2}$/TeO$_3^{-2}$ diminue avec l'augmentation de la concentration en hydroxyde alcalin de 0.1 à 2 7N, mais il reste constant pour des alcalinités plus fortes; et pour des concentrations de Te^{+4} égales à 0.09-0.02N. Te^{+4} peut être dosé au moyen de KMnO$_4$ dans NaOH 1.5 à 2N. On agite le mélange à la température ordinaire et on titre l'excès de KMnO$_4$ par un formiate.

ZUSAMMENFASSUNG

Durch Oxydation von Te^{+4} (ungefähr 0.02 bis 0.09N) mit Hilfe von Kaliumpermanganat geht das letzte quantitativ zu MnO$_2$ über, in Lösung von NaOH 0.1 bis 4N. Mit den folgenden Konzentrationen: Te^{+4} $4.585 \cdot 10^{-4}$ bis $1.834 \cdot 10^{-5}N$, KMnO$_4$ $2.096 \cdot 10^{-3}$ bis $4.192 \cdot 10^{-5}M$ und NaOH 3 bis 3.5N, erhält man eine quantitative Reduktion von Permanganat zu Manganat. Die Reduktion von KMnO$_4$ mit Te^{+4} ($4.63 \cdot 10^{-2}N$) führt zu MnO$_2$, welches von ein wenig Mn^{+3} begleitet ist; eine Bildung von Manganat findet nicht statt. In Gegenwart von Tellursäure bildet sich kein Mn^{+3} und die Reaktion ist quantitativ. Mit Te^{+4} 4.5 bis $1.13 \cdot 10^{-3}N$ beobachtet man den Übergang zu Manganat. Das Potential des Systems TeO$_4^{-2}$/TeO$_3^{-2}$ wird vermindert mit des Erhöhung der Konzentration an Alkalihydroxyd von 0.1 bis 2.7N; es bleibt aber konstant für stärkere Alkalinitäten und für Konzentrationen von Te^{+4} 0.09 bis 0.02N. Te^{+4} kann mit Hilfe von KMnO$_4$ in NaOH 1.5 bis 2 N bestimmt werden. Man rührt das Gemisch bei Zimmertemperatur um und titriert den Überschuss an KMnO$_4$ mit einem Formiat.

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CHROMATOGRAPHIE SUR PAPIER DES IONS MINÉRAUX
VIII. SÉPARATION DES CATIONS DES IONS PHOSPHORIQUES

par

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EBEL et ses collaborateurs ont montré que la chromatographie sur papier permet de séparer les méta-, ortho- et pyrophosphates[1-5]. Ces auteurs n'ont toutefois pas étudié la séparation de ces anions des cations tels que Fe^{+3}, Cu^{+2}, UO$_2^{+2}$ *etc.*, problème que se pose dans l'identification de produits radioactifs ainsi que dans divers procédés analytiques.

Dans le présent travail nous avons étudié le comportement en chromatographie sur papier des ions phosphoriques, arsénieux et arsénique en présence de différents cations. Pour beaucoup de problèmes, il suffit de considérer le comportement de l'ion orthophosphorique car les autres ions phosphoriques s'hydrolysent facilement en solution acide et peuvent être détruits avant la séparation chromatographique.

Mouvement des ortho-, pyro- et métaphosphates

La Figure 1 montre les positions de taches après développement avec du butanol saturé de HCl 1*N*. Tous les ions sauf l'orthophosphate, l'arséniate et l'arsénite, donnent des comètes considérables dues à l'adsorption ou à l'hydrolyse pendant

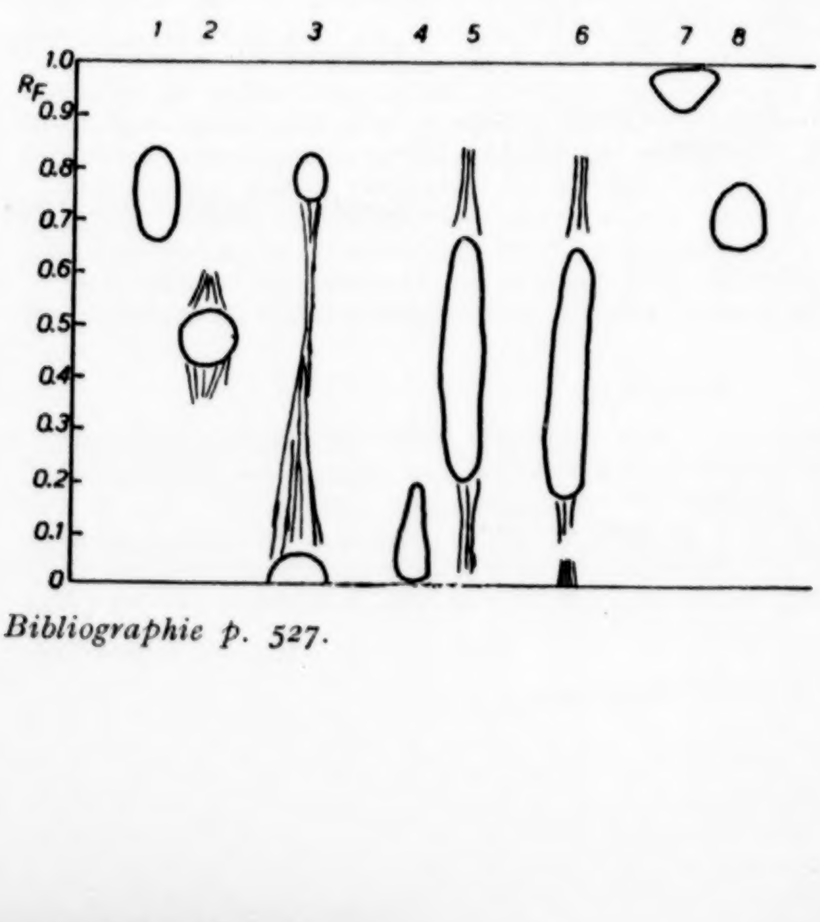

Fig. 1. Mouvement des phosphates, arsénite et arséniate avec du butanol saturé de HCl 1*N*.
1 orthophosphate
2 pyrophosphate
3 polymétaphosphate
4 tétramétaphosphate
5 tripolyphosphate
6 trimétaphosphate
7 arséniate
8 arsénite

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le développement. Dans quelques cas, le pyrophosphate donne deux taches de même intensité: l'une due au pyrophosphate et l'autre à l'orthophosphate formé au moment du développement. Il semble donc que le butanol saturé de HCl *N* ne convient pas pour séparer les différents phosphates. Par contre avec ce solvant l'orthophosphate a un R_F suffisamment élevé pour permettre sa séparation d'avec plusieurs cations.

Pour révéler les taches, on a pulvérisé sur le papier une solution de molybdate d'ammonium faiblement acide, puis une solution de $SnCl_2$ comme l'a indiqué EBEL[1]. On peut révéler l'arsénite par H_2S.

Séparation de PO_4^{-3}, Fe^{+3}, Cu^{+2} et UO_2^{+2} en quantités macroscopiques

Nous avons préparé des solutions des chlorures de fer, de cuivre, d'uranyle contenant 10 mg du cation par ml et une solution de Na_3PO_4 contenant aussi 10 mg de PO_4^{-3} par ml. Avant la chromatographie, les mélanges de ces solutions sont acidifiés avec quelques gouttes de HCl. On a chromatographié sur une même feuille de papier les solutions pures ainsi que des mélanges des solutions de cations avec la solution de phosphate de sodium. Dans aucun cas, on a observé de différence entre les R_F des solutions pures et ceux des mélanges.

Dans un essai, on a posé 0.2 ml d'une solutions contenant 2 mg de fer et 2 mg d'acide phosphorique sur une ligne tracée sur une feuille de papier. Après développement, le fer formait une zone de R_F 0.15 et l'acide phosphorique se trouvait complètement séparé à quelques cm en avant de la zone du fer. On peut donc effectuer des séparations quantitatives sur des quantités de l'ordre du mg.

Séparation de quantités impondérables d'acide phosphorique d'un mélange de cations

Pour examiner la possibilité de séparer des traces de phosphates de quantités macroscopiques de quelques métaux nous avons utilisé de l'acide phosphorique dans lequel l'atome de phosphore est radioactif, (^{32}P) ce qui permet une détection aisée.

Sur une même feuille de papier, nous avons placé une goutte de la solution du traceur $H_3P^*O_4$ pure et une goutte d'un mélange de cette solution avec une solution de $FeCl_3$. Toutes les solutions laissent environ 0.3% de leur activité au point d'application. Nous avons vérifié que cette activité est bien due à ^{32}P.

On a examiné si cette fraction d'activité est augmentée par la présence de Ca^{+2} dans la solution car d'après HANES ET ISHERWOOD[6] la formation de comètes avec les phosphates est due à la formation de sels insolubles avec les cations contenus comme impuretés dans le papier. Dans les conditions de milieu de nos expériences on n'a trouvé aucune augmentation de la fraction d'activité qui reste au point d'application. Il semble donc s'agir d'une trace d'un autre ion phosphorique que l'orthophosphate.

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La Figure 2 montre le mouvement du mélange Fe^{+3} -PO_4^{-3} et du traceur pur. On voit que la longeur de la tache de phosphate change en présence du Fe^{+3}. La Figure 3 correspond aux chromatogrammes du mélange Ca^{+2} -PO_4^{-3} et du traceur pur, sur la même feuille de papier. Ca^{+2} ne semble avoir aucune influence sur la marche du traceur.

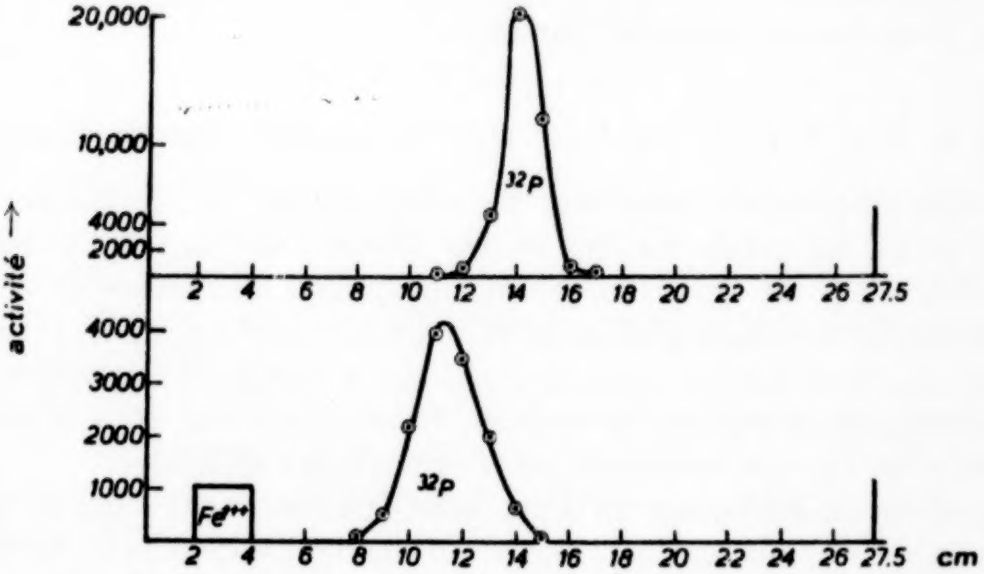

Fig. 2. Mouvement du traceur pur et du mélange Fe^{+3} - PO_4^{-3}.

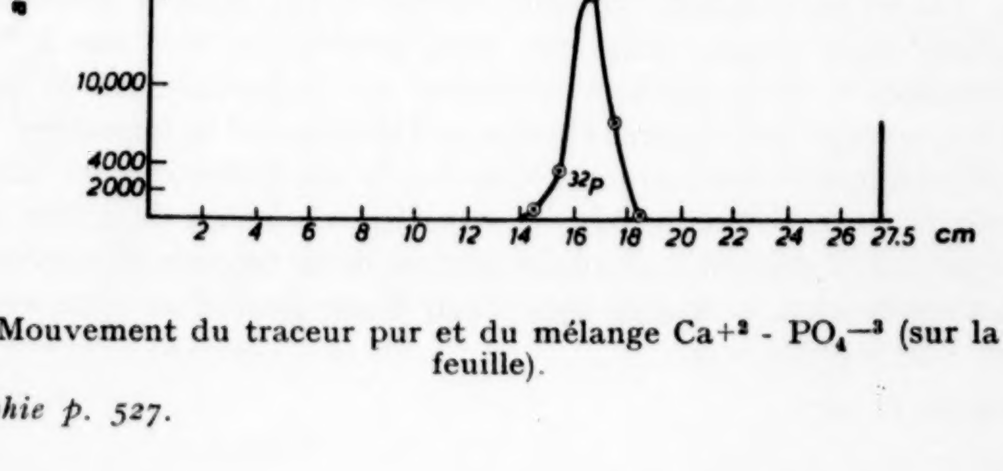

Fig. 3. Mouvement du traceur pur et du mélange Ca^{+2} - PO_4^{-3} (sur la même feuille).

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RÉSUMÉ

Le comportement des ions phosphoriques dans le butanol saturé de HCl *N* a été examiné. On peut séparer plusieurs cations de l'orthophosphate, à l'échelle des traceurs et aussi à l'échelle macroscopique.

La plupart des phosphates condensés donnent des comètes dans le solvant examiné.

SUMMARY

The behaviour of various phosphate ions in butanol saturated with *N* HCl was examined. It is possible to separate orthophosphates from various cations both in macro and microquantities. Most condensed phosphates produce comets in the solvent examined.

ZUSAMMENFASSUNG

Das Verhalten von Phosphaten bei der Papier-chromatographie mit Butanol — *N* HCl-Gemisch wurde untersucht. Trennungen von Mischungen von Orthophosphat mit verschiedenen Kationen ist möglich. Die meisten kondensierten Phosphate bilden Komete in dem erwähnten Lösungsmittel.

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PAPER CHROMATOGRAPHY OF INORGANIC IONS

IX. A NOTE ON THE PREPARATION OF CARRIER-FREE ^{131} Cs

by

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A recent paper by STEEL[1] describes the separation of Cs, Rb, K and NH_4 using phenol saturated with 2*N* HCl as solvent.

For the purpose of separating carrier-free ^{131}Cs from about 50 g of $BaCO_3$ irradiated at Harwell (activity 3 millicurie), the movement of Ba^{+2} and Sr^{+2} in phenol/2*N* HCl was examined and both were found at the point of application indicating the possibility of a satisfactory separation of Cs^+ (R_F 0.5) from Ba^{+2}.

It was necessary, however, to concentrate the Cs in a small quantity of $BaCl_2$ before placing it on the paper and two methods of concentration were tried (i) leaching the $BaCO_3$ with water and (ii) conversion of the carbonate to the chloride and precipitation of the $BaCl_2$ with conc. HCl at 0° C as previously described by FAJANS AND VOIGT[2].

Leaching the carbonate extracted only about 4% of the total activity. Hence the recrystallization of the chloride was employed and the mother liquors twice

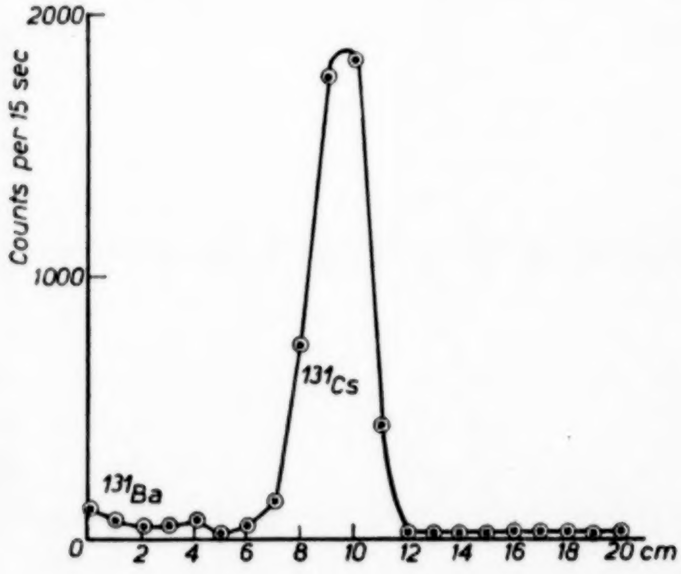

Fig. 1. Separation of ^{131}Cs from Ba with phenol saturated with 2*N* HCl. Ba round R_F = 0.

References p. 529.

concentrated and the crystals rejected till only about 0.2 ml remained. These were placed on a sheet of Whatman No. 1 paper and developed overnight with phenol/2*N* HCl. The activity was measured on the paper after development and showed the distribution depicted in Fig. 1. Fig. 2 represents the chromatogram of the carbonate leachings and the percentages extracted were estimated from the relative activities on the two chromatograms. The zone holding the peak was cut out and ashed, yielding very little residue which was dissolved in a few drops of HCl and evaporated on a support employing an infrared lamp.

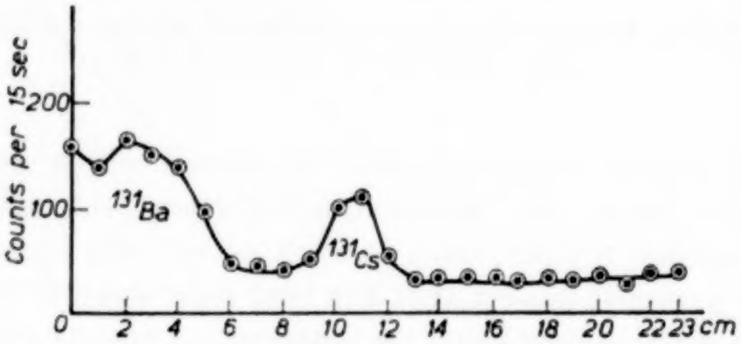

Fig. 2. Chromatogram of the leachings of activated $BaCO_3$ with distilled water (recovery about 4% of total Cs).

SUMMARY

Carrier-free ^{131}Cs was prepared by crystallization of the irradiated $BaCl_2$ and paper chromatography of the mother liquors with phenol saturated with 2*N* HCl.

RÉSUMÉ

^{131}Cs a pu être préparé par cristallisation à partir de $BaCl_2$ irradié, et chromatographie sur papier de la solution mère, au moyen de phénol saturé de HCl 2*N*.

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^{131}Cs konnte hergestellt werden durch Kristallisation von bestrahltem $BaCl_2$ und Papierchromatographie der Lösung mit Hilfe von Phenol, das mit 2*N* HCl gesättigt ist.

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ANALYSIS OF MIXTURES OF THE CONDENSED PHOSPHATES BY ION-EXCHANGE CHROMATOGRAPHY

by

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In a previous paper[1], equations were developed which describe the elution behavior of ortho-, pyro-, tri-, trimeta-, and tetrametaphosphates with Dowex 1-X10. Data regarding the pertinent constants were also presented. From Fig. 4 of this previous paper, it is seen that the best separation of the five phosphates will be achieved if the eluant has a pH between 5.0 and 7.0. At lower pH values, the log *C* value of triphosphoric acid approaches too closely to that of the tetrameta acid to permit an efficient separation. At pH values above 7.0, the log *C* values of the ortho, pyro, and tri acids come too close to each other. As indicated in this figure, the log *C* values of trimeta and tetrameta acids are independent of pH. They are also too large to permit elution in a reasonable length of time and too close to each other to permit a separation. As indicated in Table VI[1] the use of a more concentrated solution of potassium chloride as eluant would decrease the *C* values and also spread them apart sufficiently to make a separation possible. The *C* values for the meta acids approach infinity when eluants of less than $0.250M$ potassium chloride are used.

From the equations and constants previously presented, graphs were constructed to show the relationship between log *C* and the concentration of the eluant at constant pH. Two such graphs are presented in Figs. 1 and 2. With the aid of these graphs and the data of Table VI[1], separation procedures for the five lowest phosphoric acids were developed. Two schemes were worked out, one at a pH of 7.0 and the other at a pH of 5.0. It was found that the separation procedure was more satisfactory at a pH of 5.0.

It is theoretically possible to obtain a complete separation of the five phosphates with a single eluant. However, such an elution would necessitate a low eluant concentration and hence very lengthy elutions. For this reason, it was decided to use three different eluant concentrations for the separation.

The equations presented previously[1] and the data of Figs. 1 and 2 cannot be used directly to calculate the positions of the elution maxima, U^*, when different concentrations of eluant are used successively. Equations are presented below by means of which it is possible to calculate U^* under these conditions.

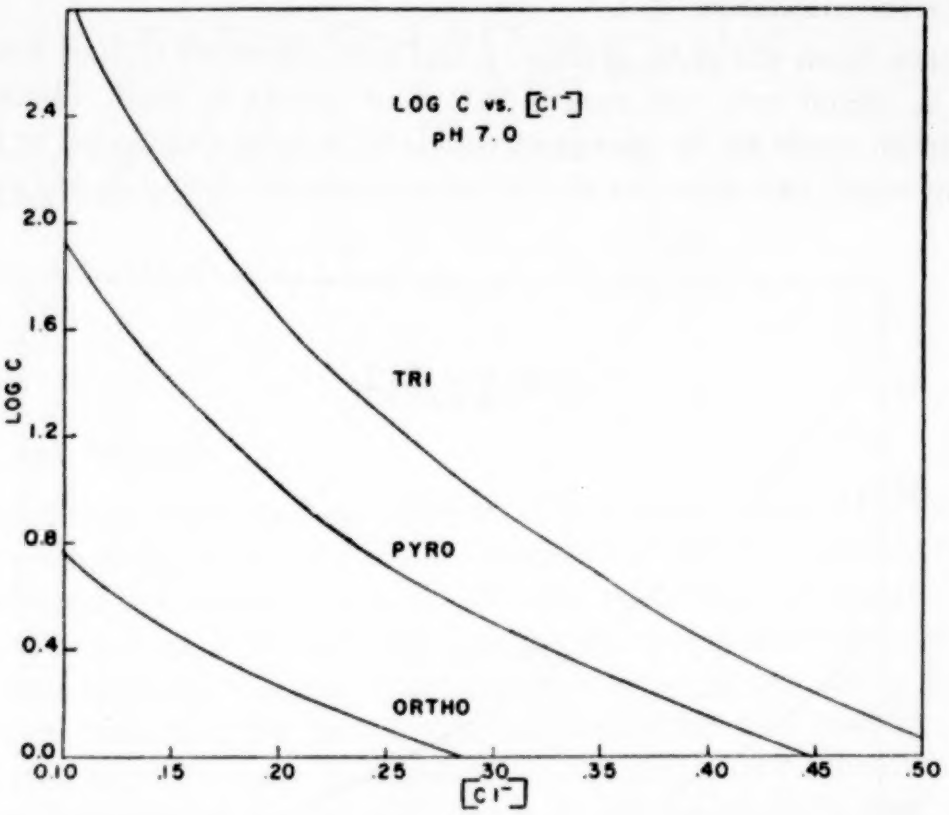

Fig. 1

Exact predictions of the best elution conditions could not be made on the basis of theoretical considerations alone because the equations and graphs presented predict only the positions of the maxima of the elution curves. In order to predict the elution conditions necessary for a quantitative separation, it would be necessary to know also the width of the elution curves. In spite of this limitation, the equations and graphs were frequently used as a guide in the choice of elution conditions, and the time required to develop a quantitative separation scheme was vastly decreased by their use.

Equation (23)[1] was used to calculate the minimum column height necessary to separate the two species most difficult to resolve, which under the chosen conditions were trimeta- and tetrametaphosphate.

DERIVATION OF EQUATIONS

Notation

The notation used in this paper in addition to that previously defined[1] follows:

C_A, C_B, C_C = the values of C if only eluant A, B, and C, respectively, is used

h_A, h_B, h_C = the fractions of the column length H travelled under the influence of eluants A, B, and C, respectively

U_A, U_B, U_C = the volumes used of eluants A, B, and C, respectively

U_A^*, U_B^*, U_C^* = the values of U^* if only eluant A, B, or C, respectively, is used

References p. 537.

Equation for the calculation of U^*

It is possible from the data of Figs. 1 and 2 to calculate C, and hence U^* for an elution in which only one concentration of eluant is used. There follows a derivation of an equation by means of which U^* can be calculated in the case of an elution in which two different eluant concentrations, A and B, are used successively.

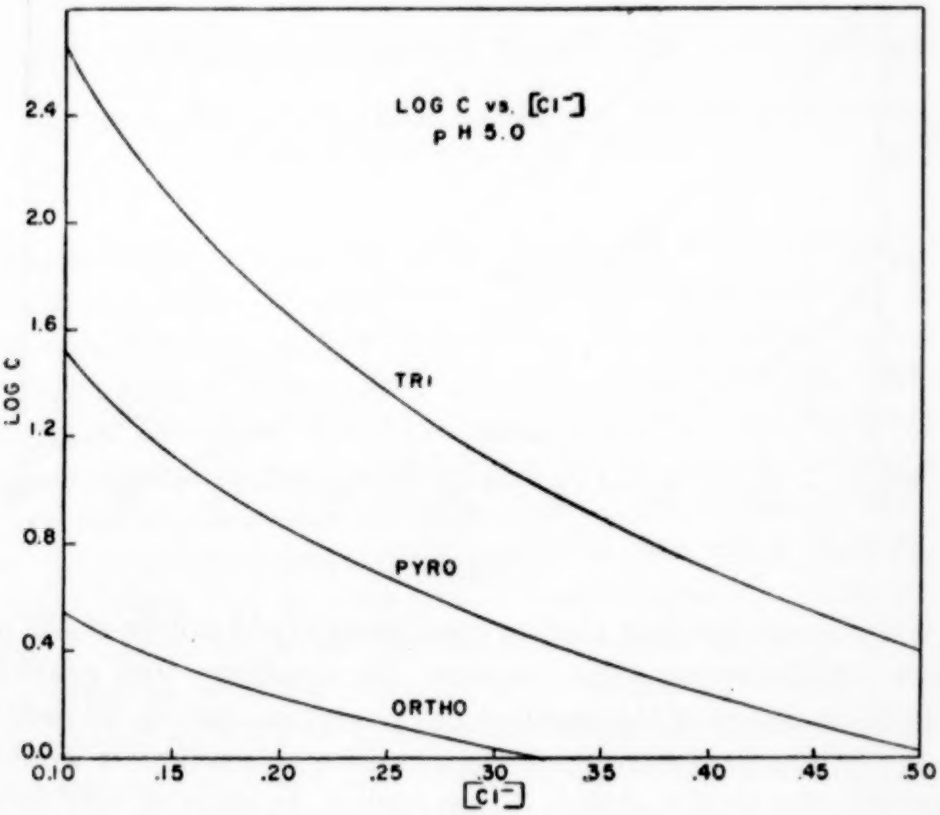

Fig. 2

If eluant A were used exclusively[1]

$$U_A^* = (C_A + 1)\ V$$

If only U_A ml of eluant A are used, the fraction h_A of H which the peak has moved is

$$h_A = \frac{U_A}{U_A^*} = \frac{U_A}{(C_A + 1)V}$$

The fraction h_B still to be travelled by the peak is

$$h_B = 1 - \frac{U_A}{(C_A + 1)V}$$

If eluant B were used exclusively

$$U_B^* = (C_B + 1)V$$

Since only the fraction h_B is still to be travelled, the volume of eluant B necessary is

$$U_B = h_B\ U_B^* = h_B\ (C_B + 1)V = (C_B + 1)\ \left(V - \frac{U_A}{C_A + 1}\right)$$

References p. 537.

The total volume of eluants A and B necessary to reach the peak is then

$$U^* = U_A + (C_B + 1)\left(V - \frac{U_A}{C_A + 1}\right) \quad (1)$$

An analogous equation was derived for an elution in which three different eluant concentrations are used:

$$U^* = U_A + U_B + (C_C + 1)\left(V - \frac{U_A}{C_A + 1} - \frac{U_B}{C_B + 1}\right) \quad (2)$$

EXPERIMENTAL

Apparatus and reagents

The ion-exchange resin used was Dowex 1-X10, 100 to 200 mesh. Two different batches of resin were used. These were designated by the manufacturer as lot 2330-15 and lot 1195, respectively. The former resin was used to prepare three columns designated as I, II and III. Column IV was prepared from the latter resin. The dimensions of each of these columns were 3.8 sq. cm × 14 cm.

The fraction collector, pH meter, spectrophotometer and reagents, including the phosphates, were the same as discussed in the previous publication[1]. The preparation and buffering of eluant solutions was also discussed in that paper. The eluant solutions used for the recommended analytical procedure were $0.250M$, $0.400M$, and $0.500M$ potassium chloride buffered to a pH of 5.0 with $0.005M$ acetate buffer. These eluants will be designated as eluants 1, 2, and 3, respectively. Analogous eluants of $0.225M$, $0.400M$ and $0.500M$ potassium chloride buffered at a pH of 7.0 will be designated as eluants 4, 5 and 6. A small quantity of mercuric iodide was added to each of the eluant solutions as a preservative. The vanadomolybdate reagent for the phosphate determinations was prepared according to the method of BARTON[2] except that twice the amount of nitric acid was used in order to hasten the hydrolysis to orthophosphate. This also produced a more stable reagent.

Preliminary elutions

The elution procedure used was the same as that previously described[1]. The fractions were collected and analysed in the same manner, and graphs of phosphate concentration *vs.* volume of eluate were prepared. An examination of these preliminary elution curves indicated what changes in elution conditions were necessary in order to perfect the separation. These preliminary elutions were carried out at a flow rate of 0.3 cm per minute. Later experiments showed that the separation was not impaired by increasing the flow rate to 0.6 cm per minute. At a flow rate of 0.9 cm per minute, however, excessive tailing and consequent overlapping of elution curves occurred.

Method of analysis

The sample never contained more than 0.15 millimole of orthophosphate, 0.075 millimole of pyrophosphate, 0.05 millimole of tri- or trimetaphosphate, and 0.038 millimole of tetrametaphosphate. It was dissolved in 2 ml of eluant 1 and eluted on the ion-exchange column, previously equilibrated with eluant 1. Eluant 1 was used for the first 220 ml; then eluant 2 was used until a total of 333 ml had been collected, and finally eluant 3 was used to complete the elution. Since different batches of resin have slightly different properties, it was necessary to cut at different points to obtain a separation. Thus for columns I, II and III, the cuts were made as follows: the first 105 ml of eluate contained all the orthophosphate. The next 115 ml contained all the pyrophosphate. The subsequent fractions of 141, 125, and 152 ml contained respectively, the tri-, tetrameta- and trimetaphosphate. For column IV fractions of 97, 143, 110, 100 and 150 ml were collected to obtain the separated phosphates in the same order. These fractions were collected in graduated cylinders and diluted with water in volumetric flasks. Appropriate aliquots were subjected to a determination of total phosphorus as previously described[1,2].

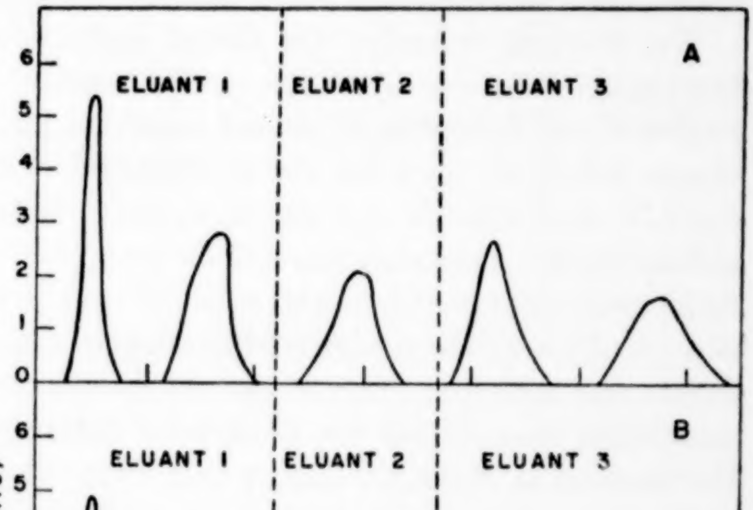

Fig. 3. Separations of the five phosphates

A. Column I Dowex 1-X10, lot 2330-15 pH = 5.0 Columns II and III gave curves very similar to graph A.

B. Column IV. Dowex 1-X10, lot 1195 pH = 5.0.

C. Column I. Dowex 3-X10, lot 2330-15 pH = 7.0.

References p. 537.

RESULTS

Elution graphs

The elution curves showing separations of the five phosphates are given in Fig. 3. Although the separation of Fig. 3 C at a pH of 7.0 is quantitative, it can readily be seen that the free volume between pyro- and triphosphate is small due to the tailing in the pyrophosphate curve. For this reason, the analytical separations were carried out at a pH of 5.0.

Application of equations (1) and (2)

In order to show the validity of equations (1) and (2), the predicted elution maxima were compared with those obtained experimentally in Fig. 3 A. These data are given in Table I.

TABLE I

TEST OF EQUATIONS (1) AND (2)

Phosphate	U^* Predicted	 Obtained
ortho	55	51
pyro	136	155
tri	306	290
tetrameta	407	429
trimeta	576	578

Analytical results

In order to test the purity of the individual phosphates used in this investigation, samples of each of the five phosphates were subjected to the foregoing analytical method. These results are listed in Table II. Each entry is the mean of three determinations. The maximum value of the mean deviation is 1.3%; and the average value, excluding those with 0.0 percentage, is 0.6%. The low value for the total phosphate found in the sample of sodium triphosphate is probably due to the presence of a small amount of high polymer, the so-called hexametaphosphate.

In order to test the accuracy of the method, mixtures containing known quantities of each of the phosphates were prepared and submitted to analysis. The results are shown in Table III. The weights of the added phosphates were corrected for impurities by the use of Table II. The values reported for mixtures 1 and 2 are the mean of duplicate determinations. The average deviation from the mean was 0.1%. Each value given for mixture 3 is the result of a single analysis. The average error for all three mixtures without regard for sign is 0.2%.

TABLE II

ANALYSIS OF INDIVIDUAL PHOSPHATES

Phosphate Taken	Per cent. of total P present as Ortho	Pyro	Tri	Tetrameta	Trimeta	Total
K_2HPO_4	99.9	0.0	0.0	0.0	0.0	99.0
$Na_4P_2O_7$	3.6	95.7	1.7	0.0	0.0	101.0
$Na_5P_3O_{10}$	1.7	5.0	88.8	0.9	0.0	96.4
$Na_4P_4O_{12}$	1.2	0.5	1.5	96.5	0.6	100.3
$Na_3P_3O_9$	3.0	1.6	0.0	0.0	95.3	99.9

TABLE III

ANALYSIS OF MIXTURES OF SODIUM PHOSPHATES

	Mixture 1 58.6 mg Columns II and III		Mixture 2 68.3 mg Columns I and IV		Mixture 3 56.7 mg Column I	
Phosphate	Taken %	Found %	Taken %	Found %	Taken %	Found %
K_2HPO_4	31.7	31.7	25.0	25.0	25.9	26.3
$Na_4P_2O_7$	22.2	22.2	19.0	19.0	20.1	20.3
$Na_5P_3O_{10}$	17.1	16.5	20.4	20.2	18.3	18.0
$Na_4P_4O_{12}$	14.5	14.3	21.0	21.0	16.1	15.9
$Na_3P_3O_9$	14.5	14.3	14.6	14.5	19.6	19.4
Total	100.0	99.0	100.0	99.7	100.0	99.9

DISCUSSION

Two schemes for separating the salts of orthophosphoric acid and its four lowest polymers have been presented. One of these has been applied to the analysis of mixtures of such phosphates. The analytical results indicate that the method is subject to a mean error of 0.2%. It is believed that this error is due largely to the limited accuracy of the colorimetric method, and not to the chromatographic technique.

The differences in the elution curves A and B of Fig. 3 indicate that different batches of resin show slightly different behavior. It is necessary therefore to test each column by analyzing the eluate in small fractions to determine at which volumes the eluate should be cut. If a separation is not obtained the first time, a minor modification in column length or the eluate volume at which the eluant concentration is changed usually corrects this difficulty.

References p. 537.

If it is known that the samples to be analyzed do not contain all of the five constituents, it is possible to simplify the procedure considerably. Thus, for samples containing only ortho-, pyro- and triphosphate, a separation with a column only 6 cm in length has been obtained. The eluant used was 0.20M potassium chloride buffered to a pH of 7.0. A simplified separation of mixtures containing only the metaphosphates has been previously reported[1].

It has been found that if hexametaphosphate is present in the sample it adheres tenaciously to the resin thus rendering the column unfit for further use if appreciable amounts are accumulated. The work is being continued in an attempt to overcome this difficulty.

ACKNOWLEDGEMENT

The authors are indebted to the United States Atomic Energy Commission for financial assistance in this investigation, and to EDWARD R. ALLEN for calling their attention to the need for a satisfactory method for the analysis of mixtures of polyphosphates.

SUMMARY

A method is presented by means of which each constituent of a mixture of ortho-, pyro-, tri-, trimeta-, and tetrametaphosphate can be separated and determined. Duplicate determinations of all five constituents can be completed in 5 hours. Each constituent was determined with a mean error of 0.2% of the sample.

The theory of ion-exchange chromatography is further developed to permit the calculation of the positions of the elution maxima when eluants of different concentrations are used successively.

RÉSUMÉ

Les auteurs proposent une méthode permettant de séparer et de doser chaque constituant d'un mélange d'ortho, de pyro, de tri, de triméta et de tétramétaphosphates. Une double détermination de ces cinq constituants peut être effectuée en 5 heures. L'erreur moyenne obtenue est de 0.2%. La théorie de la chromatographie d'échange est ensuite développée pour pouvoir calculer les positions des maxima d'élution lorsque des éluants de différentes concentrations sont utilisés successivement.

ZUSAMMENFASSUNG

Die Autoren schlagen eine Methode vor, welche es ermöglicht, die einzelnen Komponenten eines Gemisches von Ortho-, Pyro, Tri-, Trimeta- und Tetrametaphosphaten abzutrennen und zu dosieren. Eine zweifache Bestimmung dieser fünf Bestandteile kann in fünf Stunden ausgeführt werden. Der mittlere Fehlerwert, der erhalten wurde, ist 0.2%. Die Theorie der Austauschchromatographie wird dann gegeben für die Berechnung der Stellen der Elutions-Maxima bei sukzessiver Anwendung der Eluierungsmittel in verschiedenen Konzentrationen.

REFERENCES

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ANALYTICAL METHODS USED IN STUDIES ON CONTINUOUS SEPARATION OF IONS BY COUNTERCURRENT ION EXCHANGE

by

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During an investigation of the feasibility of continuous ion separation by means of countercurrent contact between ion exchange resin and solution[3,4], it became apparent that evaluation of the experimental results in terms of ion concentrations in the solution and on the resin, would be considerably enhanced by a careful study of the analytical procedures involved. The present paper describes the analytical methods used, the problems which were encountered, and how they were solved.

In order to simplify theoretical problems as much as possible, lithium ion (Li^+) and potassium ion (K^+) were chosen as the ions to be separated, and hydrogen ion (H^+) as the carrier and elutant. This particular system was selected because: (1) the three ions are of equal valence, thus simplifying the exchange mechanism; (2) Li^+ and K^+ are both available in pure form, as the chlorides, at reasonable costs: (3) as the second and fourth elements in the alkali metal series, Li^+ and K^+ differ sufficiently to make separation feasible; and (4) H^+ may be analysed easily. A nuclear-sulfonic polystyrene-base type resin, Chempro C-20 cation exchanger, was used because of its homogeneity of structure and uniform exchange strength.

The objectives of the analytical program, then, were (1) the accurate determination of the concentrations of the alkali metal ions in solution in the presence of H^+ and each other, and (2) the quantitative removal of the alkali metal ions from the resin in a form suitable for solution analysis.

ANALYSIS OF SOLUTIONS

The flame photometer was chosen for the analysis of the Li^+ and K^+ because it offered the highest potential (and speed) available for analysis of the alkali metal ions in the concentration range of interest[1,2,3]. A Beckman DU spectrophotometer with an acetylene-oxygen flame attachment was used throughout the program.

The four primary variables that might affect the analytical results were the wavelengths and slit widths used for the two ions and the concentrations of the interfering alkali metal ions and hydrogen ion. As suggested by the instrument manufacturer, the wavelengths of the principal lines (on this instrument, 771 mμ for the potassium and 673 mμ for the lithium) were used throughout. In all of the tests involving the other variables, Li^+ or K^+ solutions containing 1.0*N* HCl were used as the standard. These were prepared at 0.01, 0.05, 0.1, and 0.5*N*, by weighing out the salt, dissolving in water and diluting to volume, and then checking the standardization gravimetrically through precipitation of the chloride with silver nitrate solution. At least five dilutions of each of the above primary standards were then made up by diluting aliquots with hydrochloric acid and water so that the final solutions were 1.0*N* with respect to the hydrogen ion.

In general, the calibration procedure consisted of, first, adjusting the instrument to the chosen settings of wavelength and slit width for the ion concerned. The primary standard was then aspirated into the flame and the photometer set to a reading corresponding to 100% transmission. The relative transmissions of the diluted solutions were then determined and plotted against the actual concentration of the ion of interest. This plot was then considered the calibration curve for that particular primary standard. Fig. 1 is an example of a calibration curve for pure potassium ion.

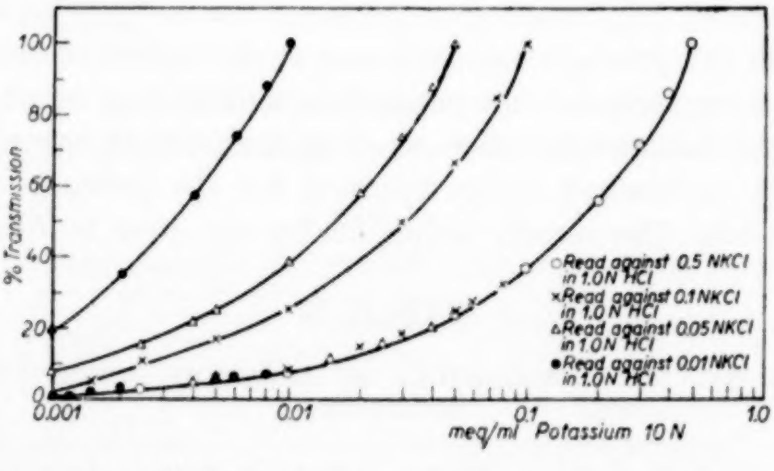

Fig. 1. Sample calibration curve for potassium ions in 1.0*N* HCl

In order to see if these curves were consistent with each other, the reading for 100% transmission on each curve was dropped to the bottom curve (as read against 0.5*N* solution) and all other points on each graph corrected proportionally. When this was done, the points shown on the bottom curve are obtained and it is seen that they are self-consistent.

Effect of slit width. The effect of slit width could not be checked directly since it was necessary, first, to find the proper slit width to be used with each of the primary standards mentioned above. At too small a slit width, the sensitivity became poor because so little of the flame intensity reached the instrument; when the slit width was too large, the interference from other ions became greater. Thus, the proper slit width had to be based on an optimum balance of these two factors. The optimum values obtained for this instrument are given in Table I.

TABLE I

OPTIMUM SLIT WIDTHS FOR VARIOUS CONCENTRATIONS OF LITHIUM AND POTASSIUM IONS USING THE BECKMAN DU SPECTROPHOTOMETER WITH A FLAME PHOTOMETER ATTACHMENT

Actual normality of Li^+ and K^+ in 1.0*N* HCl	Optimum slit width (mm) Li^+	K^+
0.01	0.15	0.06
0.05	0.15	0.06
0.1	0.08	0.04
0.5	0.05	0.02

As might be expected, the optimum slit width depended on the strength of the flame line, and thus on both the ion and its approximate ionic concentration. The actual effect of slit width was best shown by rechecking one of the primary standards, and its dilutions, on the flame photometer with the slit width set higher than optimum. For comparison purposes the instrument was set at 100% transmission with the primary standard and at the optimum slit width. The slit width was then increased and the percent transmission of all of the samples was determined. These values were then used to read the indicated concentrations from the normal calibration curve obtained for the primary standard at the optimum slit width. The results indicated by the new readings are given in Table II.

TABLE II

EFFECT OF SLIT WIDTH VARIATION ON APPARENT CONCENTRATIONS OF SOLUTIONS

Actual normality of Li^+ and K^+ in 1.0*N* HCl	Ratio of indicated to actual normality Li^+ at 0.2 mm slit width	K^+ at 0.1 mm slit width
0.005	1.01	No reading
0.010	1.08	1.09
0.020	1.17	1.01
0.030	1.15	1.04
0.040	1.13	0.96
0.050	1.01	0.98

These values again confirm the fact that, at larger slit widths, extraneous interferences ("background") have a greater effect on the results.

References p. 549.

Effect of presence of hydrochloric acid. It very quickly became apparent that the hydrochloric acid, always present in the experimental solutions, also interfered with the readings for the metal ions. This effect had also been reported by PARKS, JOHNSON AND LYKKEN[5]. For this reason it was decided to check the magnitude of this effect. Standard solutions of 0.01*N* KCl and 0.01*N* LiCl were prepared by weighing out the pure salt, dissolving in distilled water, and diluting to volume with water. The concentrations were checked as before by precipitating the chloride ion with silver nitrate. Aliquots of the standard solutions were diluted with distilled water to volume to give four different concentrations. These solutions were then used to prepare a special calibration curve for the flame photometer. Regular acid-containing standards were then checked on the flame photometer against this calibration curve, using the optimum slit widths given above. The results are shown in Table III.

TABLE III

EFFECT OF WATER-CONTAINING *vs.* ACID-CONTAINING STANDARDS ON APPARENT CONCENTRATIONS OF SOLUTIONS

Actual normality of K^+ or Li^+ in 1.0*N* HCl	Ratio of indicated to actual normality	
	Li^+	K^+
0.002	1.07	1.13
0.004	1.06	1.12
0.006	1.06	1.12
0.008	1.06	1.12

It is apparent that the use of standards in water, rather than in 1.0*N* hydrochloric acid, will give high readings on the experimental samples.

TABLE IV

MUTUAL INTERFERENCE OF LITHIUM AND POTASSIUM IONS

Actual normality of Li^+ in 1.0*N* HCl	Ratio of indicated to actual normality		
	$3Li^+:1K^+$	$1Li^+:1K^+$	$1Li^+:3K^+$
0.001		1.00	1.00
0.002		1.03	1.01
0.003	1.02		
0.004		1.05	1.05
0.006	1.02	1.04	1.04
0.008		1.01	1.04
0.010		1.01	1.02
0.012	1.02		
0.018	1.05		
0.024	1.02		
0.030	1.01		
0.10		0.87	
0.20		1.11	
0.30		1.15	
0.40		1.12	

References p. 549.

Effect of mutual interference of alkali ions. Li^+ and K^+ exhibited mutual interference, and the effect of this interference was evaluated by the preparation of standard solutions, in 1.0*N* hydrochloric acid, containing both K^+ and Li^+ in 1:1, 3:1, and 1:3 ratios, and at various concentration levels. Readings were then obtained against the pure K^+ or Li^+ calibration standards. Some of the Li^+ results are given in Table IV.

This information indicates that the greater quantities of K^+, either ratio-wise or concentration-wise, usually caused increased interference in the Li^+ results. This effect is shown in Fig. 2.

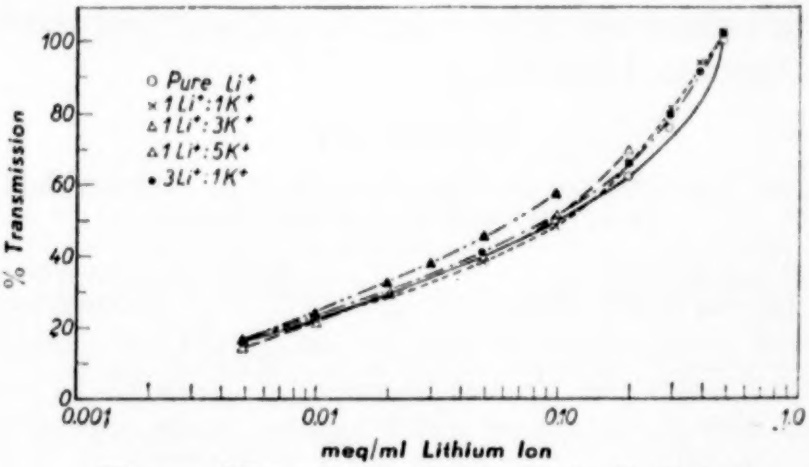

Fig. 2. Mutual interference of alkali ions

A comparison of these results with those for K^+ indicate that Li^+ cause less interference with the K^+ readings than K^+ with Li^+. For example, in the case of 1 Li^+:1 K^+, the results are given in Table V.

TABLE V

LITHIUM INTERFERENCE WITH POTASSIUM IONS

Actual normality of Li^+ or K^+ in 1.0*N* HCl	Ratio of indicated to actual normality	
	Li^+	K^+
0.001	1.00	1.01
0.002	1.03	1.00
0.004	1.05	1.01
0.006	1.04	1.01
0.008	1.01	0.99

Adopted procedure. The procedure which was finally adopted for the analysis of the solutions encountered in the countercurrent ion exchange studies is outlined below:

The volume of the sample is recorded and the acid content determined on an aliquot. If the H^+ concentration is more than 5% below 1.0N, hydrochloric acid is added to a second aliquot to make the solution 1.0N, and the new volume recorded. The K^+ and Li^+ concentration are determined on the acid-adjusted sample with a flame photometer at predetermined wavelengths using the proper reference solutions. The amounts of K^+ and Li^+ are obtained by reference to the proper calibration curves.

Preliminary values for K^+ and Li^+ were obtained from the calibration curves of the pure ions. The approximate ratio of K^+ to Li^+ was then determined from these results and the corrected K^+ and Li^+ values read from the proper ratio calibration curve.

The calibration curves were prepared by plotting readings obtained on solutions of lithium chloride and potassium chloride in 1.0N HCl in molar ratios of $Li^+ : K^+$ of 0:1, 1:1, 1:2, 1:5, 3:1, 5:1, and 1:0. Solutions of 0.5N KCl, 0.1N KCl, 0.05N KCl, 0.01N KCl, 0.5N LiCl, 0.1N LiCl, 0.05N LiCl, and 0.01N LiCl were used as reference standards.

REMOVAL OF IONS FROM RESIN

In the case of resin* analysis, the principal problem was the quantitative transfer of potassium and lithium from the resin sample to a solution which can be analysed by the standard procedure established above. The removal methods tested fell into two general categories: (1) elution with an excess of another ion, and (2) degradative oxidation of the resin followed by an acid leach of the residue.

In the elution method, an aliquot of the resin sample was transferred to a tube, and the chosen volume of elutant was passed through it at a slow rate. The resin was then washed with distilled water, and the combined effluents were analysed for the K^+ and Li^+ removed from the resin. The resin aliquot was then oven-dried, so that the concentrations could be expressed on a consistent basis of dry hydrogen-form resin. Since the amount of alkali metal ion originally present on the resin was not known, each set of tests was performed on aliquots of the same resin sample so that the results could be compared.

Effect of elution conditions. The elution experiments involved the effect of elutant quantity and concentration. Each of the elution columns used to check the treatments contained 10 g of oven-dried resin. The results obtained are given in Table VI.

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* The resin used in this work was a polystyrene-sulfonic acid type resin C-20 manufactured by Chemical Process Company, Redwood City, California.

TABLE VI

EFFECT OF ELUTANT CONCENTRATION ON QUALITY OF EFFLUENT

Elution treatment[a]	Amount removed, meq/g	
	Li^+	K^+
100 ml 1.0*N* HCl	0.078	0.094
200 ml 1.0*N* HCl	0.077	0.137
400 ml 1.0*N* HCl	0.078	0.160
100 ml 2.0*N* HCl	0.079	0.158
400 ml 2.0*N* HCl	0.078	0.159
1000 ml 2.0*N* $CuCl_2$	0.073	0.140

[a] The elutant was passed through the resin at a superficial velocity of about 5 ml/min.

It appears that either 400 ml of 1.0*N* HCl or 100 of 2.0*N* HCl would elute both K^+ and Li^+ from the resin satisfactorily. The copper chloride elutant was not satisfactory, mainly because it caused interference in the flame photometer readings. A volume of 125 ml of 2.0*N* HCl was selected as best for the elution procedure, because the resin could be washed with an equal volume of distilled water and yield just 250 ml of effluent (a standard volumetric flask size) at a hydrochloric acid concentration of 1.0*N*, the desired level for analysis.

Effect of dry-ashing conditions. The second removal method, destruction of the resin, was accomplished either by dry-ashing or by chemical oxidation (wet-ashing).

The resin samples were oven-dried prior to these destructive treatments so that the results could be expressed on a dry basis. In the dry method, the resin was carefully pyrolysed at 1000° C until only a mineral ash remained. After cooling, this ash was then taken up with 1.0*N* HCl and the solution analysed as usual. The wet method consisted of treating the resin with nitric acid and sulfuric acid, and in some cases perchloric acid, at the boiling point until no residue was apparent. The resultant solution was then evaporated to dryness, taken up with 1.0*N* HCl, and analysed as before.

Again, each set of tests was performed on aliquots of the same resin sample so that the results could be compared. The first experiments compared the elution method with dry-ashing in porcelain crucibles.

TABLE VII

COMPARISON OF ELUTION METHOD WITH DRY-ASHING OF RESIN

Treatment	Amount found, meq/g	
	Li^+	K^+
Resin eluted with 100 ml of 2.0*N* HCl	0.079	0.158
Resin ashed at 1000° C	0.024	0.025
20 ml 0.01*N* Solution of $1Li^+ : 1K^+$	None	None

As can be seen in Table VII, ashing in porcelain is completely unsatisfactory, probably because the Li^+ and K^+ are taken up in the porcelain glass.

Next, for comparison, platinum crucibles were tried for the dry-ashing instead of porcelain crucibles. In some cases, solutions containing known quantities of Li^+ and K^+ were added to the ashing containers before treatment. In these cases, the results should be high by the amount added. The results of these tests are given in Table VIII.

TABLE VIII

COMPARISON OF DRY-ASHING RESULTS IN PORCELAIN AND IN PLATINUM

Treatment	Amount, meq/g			
	Predicted		Found	
	Li^+	K^+	Li^+	K^+
Resin eluted with 100 ml of 2.0*N* HCl			0.079	0.158
Resin ashed in porcelain at 1000° C			0.024	0.025
Resin ashed in platinum at 1000° C			0.083	0.157
Resin plus known solution in platinum at 1000° C	0.202	0.271	0.188	0.256
Known solution ashed in platinum at 1000° C	0.380*	0.338*	0.075*	0.025*

* Concentrations are given in total meq rather than meq/g.

Although the platinum crucibles are much more satisfactory than porcelain, poor recoveries of added solutions were obtained. This may be due to volatilization or to background effect on the flame caused by fine particles of incompletely ashed resin.

Effect of wet-ashing conditions. The wet-ashing technique was tried next. In these experiments some of the treatments were repeated several times to check the reproducibility of the results. In all cases the material was treated with nitric acid and sulfuric acid, at the boiling point, until the solution was essentially clear. These results are given in Table IX.

The wet-ashing method appears to give fairly reproducible results, but poor recoveries of the added solutions were obtained. Again volatilization or flame background interference due to unreacted resin constituents may be the cause.

A second series of wet-ashing experiments was undertaken next. In this series perchloric acid was used, in addition to nitric acid and sulfuric acid. A few elution runs were also included for comparison purposes on the new resin aliquot. As before, the experiments were performed in replicate.

TABLE IX

TABULATION OF WET-ASHING EXPERIMENTS

	Amount, meq/g			
Sample	Predicted		Found	
	Li^+	K^+	Li^+	K^+
Resin			0.103	0.168
Resin			0.090	0.185
Resin			0.093	0.183
Resin			0.089	0.175
Resin			0.093	0.183
Resin plus known solution	0.172	0.231	0.156	0.237
Resin plus known solution	0.206	0.271	0.213	0.266
Resin plus known solution	0.179	0.237	0.163	0.233
Resin plus known solution	0.202	0.255	0.185	0.259
Resin plus known solution	0.165	0.226	0.146	0.220
Resin plus known solution	0.254	0.295	0.264	0.275
Resin plus known solution	0.245	0.351	0.260	0.256
Resin plus known solution	0.314	0.343	0.329	0.315
Resin plus known solution	0.274	0.311	0.240	0.301
Known solution*	0.860	0.676	0.710	0.668
Known solution*	0.860	0.676	0.710	0.688
Water	None	None	None	None
Water	None	None	None	None
Resin eluted with 100 ml of 2.0*N* HCl			0.079	0.158

*Concentrations are given in total meq rather than in meq/g.

TABLE X

WET-ASHING IN THE PRESENCE OF PERCHLORIC ACID

	Amount, meq/g			
Sample	Predicted		Found	
	Li^+	K^+	Li^+	K^+
Resin			0.055	0.138
Resin			0.056	0.142
Resin			0.059	0.140
Resin			0.058	0.142
Resin			0.059	0.141
Known solution*	0.500	0.500	0.460	0.485
Resin eluted with 100 ml 2.0*N* HCl			0.066	0.143
Resin eluted with 100 ml 2.0*N* HCl			0.068	0.145

*Concentrations are given in total meq rather than in meq/g.

Although Table X shows fairly good agreement in this wet-oxidation method, elution is simpler and faster.

Adopted procedure. A 25 ml (8.0 g) sample of the resin is placed in a column 1/2 × 7 inches and eluted with 125 ml of 2*N* hydrochloric acid at a rate of 5 ml per minute, catching the effluent in a 250 ml volumetric flask. The sample of resin is then washed with distilled water in the same manner, adding the wash effluent to the acid effluent in the volumetric flask. The solution is diluted to exactly 250 ml with distilled water and analysed as outlined in the analysis of solutions. The resin is transferred to a beaker, dried overnight at 105° C and weighed. The results are calculated on a milliequivalent per gram dried resin basis.

Determination of the ultimate exchange capacity of the resin.

An important factor in ion exchange studies is the ultimate capacity, or total exchange capacity, of the ion exchange resin. It is a measure of the number of positions available for exchange in a given quantity of resin. Since its determination involves the measurement of a resin concentration the techniques involved are similar to those for the removal of ions from a resin.

Two fundamentally different methods for determining ultimate capacity were evaluated. In one, resin in the hydrogen form was converted to a metal ion form by contact with a large excess of metal salt solution. The amount of H^+ displaced from the resin into the solution was determined by titration, thereby indicating the capacity of the resin.

The alternative method involved the incremental titration of a hydrogen resin slurry with sodium hydroxide to obtain a titration curve. The amount of sodium hydroxide solution required to titrate to the point at which the pH changes rapidly, upon the addition of base, was converted to the H^+ present and thus to the ultimate capacity of the resin.

In the elution procedure a quantity of resin was first converted almost completely to the hydrogen form by extensive elution with hydrochloric acid in a fixed bed. This resin was thoroughly mixed and eluted further with $2N$ HCl. Finally it was washed with distilled water until the effluent was neutral to methyl orange. After further mixing, the resin was divided into eight portions of about 25 ml (10 g) and treated as follows:

(1) Two aliquots were transferred to small glass columns, and one liter of saturated sodium chloride solution was passed through each. The resin samples then were washed with distilled water. Aliquots of the effluent solutions were titrated with standard sodium hydroxide to the phenolphthalein end-point to obtain the quantity of H^+ released by the resin. The resin samples were treated with 250 ml $2.0N$ HCl, washed with distilled water, and dried overnight at 105° C to obtain the ultimate capacity in terms of the dry weight of hydrogen form resin.

(2) Two aliquots were treated as in procedure (1) except that two liters of saturated sodium chloride solution were used.

(3) Two aliquots were similarly treated with one liter each of 5% calcium chloride solution.

(4) Two aliquots were titrated in increments to pH 14 with standard sodium

hydroxide. The resin was back-titrated with standard hydrochloric acid. The resin samples were washed with distilled water and dried overnight at 105° C.

The results of these tests are given in Table XI.

TABLE XI

COMPARISON OF METHODS FOR ULTIMATE CAPACITY DETERMINATIONS

Treatment	Ultimate capacity, meq/g
One liter saturated NaCl	5.16
One liter saturated NaCl	5.18
Two liters saturated NaCl	5.14
Two liters saturated NaCl	5.08
One liter 5% $CaCl_2$	5.14
One liter 5% $CaCl_2$	5.08
Titration to pH 14	5.00
Titration to pH 14	5.10
Average	5.11

In the sodium hydroxide titration procedure, the break in the pH curve occurred between pH 7 and pH 11, as is shown in Fig. 3. The reverse titration with hydrochloric acid to pH 2 did not give a satisfactory end-point. No definite break was observed, and the apparent end-point resulted in an erroneously high capacity.

The procedure selected as the standard method was that of using one liter of 5% calcium chloride solution. This method was economical of the analyst's time and of reagents and gave satisfactorily reproducible results.

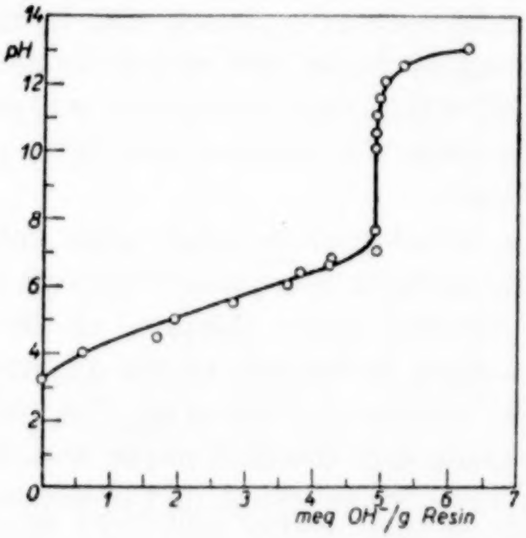

Fig. 3. Determination of ultimate capacity by incremental titration

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References p. 549.

SUMMARY

The hydrogen ion concentration exhibited a pronounced effect on the apparent alkali ion concentrations as determined with a Beckman DU spectrophotometer with a flame attachment. Lithium and potassium ions showed a mutual interference, which appeared small, but was sufficient to affect the theoretical evaluation of exchange systems, especially under trace conditions. Control of slit widths eliminated some of the interferences, but further corrective measures had to be applied by the use of prepared calibration curves.

Several methods for removing ions quantitatively from the resins were explored. While copper salts were effective elutants, they could not be used in routine analysis because of interference with the lithium and potassium ions analyses and elution with hydrochloric acid was finally chosen.

A simple and economical method was found for determining the ultimate capacity of the resin.

RÉSUMÉ

La concentration en ions hydrogène a une forte influence sur la concentration apparente des ions alcalins, déterminée au spectrophotomètre de flamme Beckman DU. Les ions lithium et potassium présentent une mutuelle interférence, qui, bien que faible, est suffisante pour fausser l'évaluation théorique des systèmes d'échange, spécialement lorsqu'il s'agit de traces. Certaines interférences peuvent être éliminées par un contrôle de l'ouverture de la fente, mais l'emploi de courbes d'étalonnage, est nécessaire. Différentes méthodes furent essayées pour l'élimination quantitative d'ions dans des résines. Bien que les sels de cuivre soient efficaces comme éluants, ils ne peuvent être utilisés pour des analyses en série car ils gênent les dosages de lithium et potassium. Il est plus avantageux d'utiliser l'acide chlorhydrique. Une méthode simple et pratique est utilisée pour la détermination de la capacité finale des résines.

ZUSAMMENFASSUNG

Die Konzentration der Wasserstoffionen hat einen grossen Einfluss auf die scheinbare Konzentration an Alkaliionen, welche mit dem Flammen-Spektrophotometer Beckman DU bestimmt wird. Die Ionen von Lithium und Kalium zeigen eine gegenseitige Interferenz, welche, obwohl sie sehr schwach ist, ausreicht, um die theoretische Bewertung des Austausch-Systemes zu stören, speziell sofern es sich um Spuren handelt. Gewisse Interferenzen können vermieden werden durch Kontrolle der Öffnung, aber die Verwendung von Eichkurven ist notwendig. Verschiedene Methoden wurden versucht für die quantitative Entfernung der Ionen aus Harzen. Obwohl die Kupfersalze wirksame Eluierungsmittel darstellen, können sie für Serienanalysen nicht verwendet werden, da sie die Bestimmung von Lithium und Kalium stören. Es ist vorteilhafter die Salzsäure zu verwenden. Eine einfache und praktische Methode wird verwendet für die Bestimmung der Kapazität von Harzen.

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THE SEPARATION OF STEREOISOMERIC INORGANIC COMPOUNDS BY PAPER CHROMATOGRAPHY

by

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The separation of cis and trans isomers of dinitrobis(ethylenediamine)cobalt(III) nitrate, dinitrobis(ethylenediamine)cobalt(III) iodide and dichlorobis(ethylenediamine)cobalt(III) chloride by paper chromatography

The separation of inorganic complex compounds which exist in *cis* and *trans* stereoisomeric forms and the resolution of the racemic compounds into their optically active components has not been accomplished so far by means of paper chromatography.

We have prepared dinitrobis(ethylenediamine)cobalt(III) nitrate, dinitrobis (ethylenediamine)cobalt(III) iodide and dichlorobis(ethylenediamine)cobalt(III) chloride by methods previously described and have obtained the pure *cis* and *trans* isomers by fractional crystallization. Each isomer in turn was passed along strips of chromatographic paper and it was thus established that both isomers differ considerably in their R_F values. The same difference was obtained by the chromatographic separation of the synthetic mixtures of both stereoisomers. In the cases studied *cis* isomers had greater R_F values than the *trans* forms.

Paper chromatography can be used with accuracy as an analytical method for the separation of inorganic complex *cis-trans* compounds and also as a convenient procedure for following the course of conversion of one isomer into the other.

Finally it is worth mentioning that the racemic complex compounds can be resolved into their optically active components by adding an optically active compound to the solvent used in the process of chromatography. The results of these investigations will be published in our next communication.

References p. 553.

EXPERIMENTAL PART

All the separations were carried out on Whatman paper No. 1 by the method of ascending chromatography. Ammonium sulphide was used as the colour reagent. The temperature during the separations was 20—22° C.

Dinitrobis(ethylenediamine)cobalt(III) nitrate[1,2,3]

Analysis for $[(NO_2)_2Co\ en_2]\ NO_3$. Co was determined as $CoSO_4$. Found: *cis* form; Co, 17.83%; *trans* form; Co, 17.72%; calculated: Co, 17.69%.

Solvent mixture: 65 ml of acetone + 30 ml of water + 5 ml of HNO_3 (sp.gr.1.42).

Time of separations: 22 hours.

R_F *cis* = 0.73 (Fig.1,I); R_F *trans* = 0.62 (Fig. 1, III); mixture of *cis* and *trans*: Fig. 1, II.

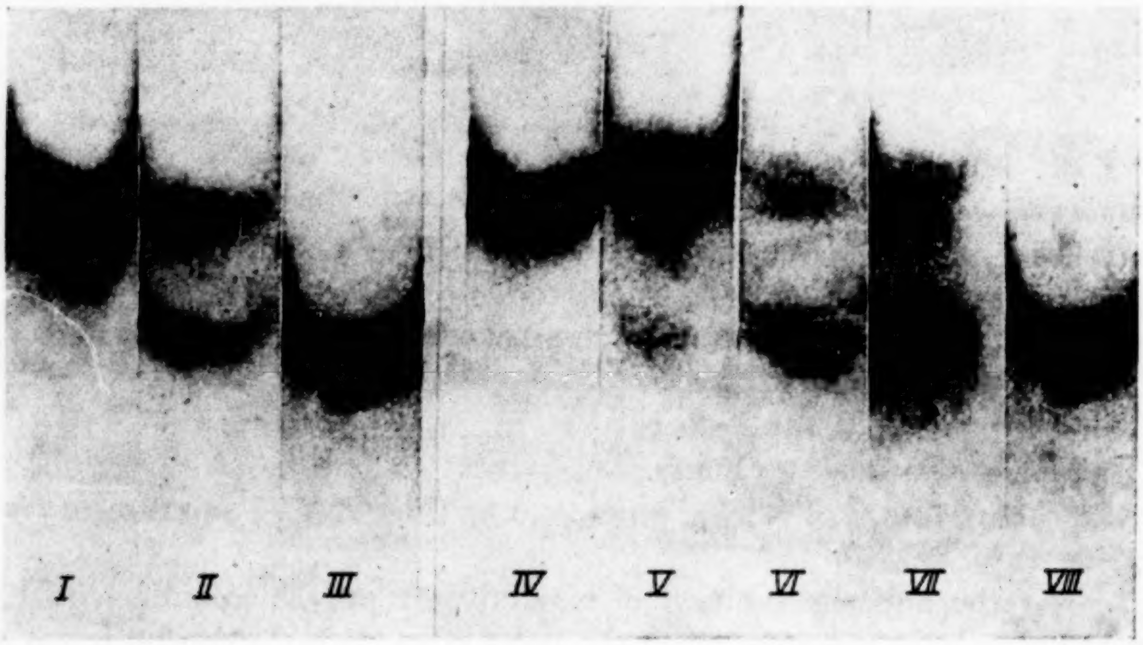

Fig. 1.

Dinitrobis(ethylenediamine)cobalt(III) iodide[1,2]

Analysis for $[(NO_2)_2Co\ en_2]$ I. Co was determined as $CoSO_4$. Found: *cis* form; Co, 14.76%; *trans* form; Co, 14.93%; calculated: Co, 14.81%.

Solvent mixture: 85 ml of acetone + 15 ml of water + 1 g of solid KI.

Time of separations: 22 hours.

R_F *cis* = 0.66 (Fig. 2, I); R_F *trans* = 0.45 (Fig. 2, III); mixture of *cis* and *trans*: Fig. 2, III.

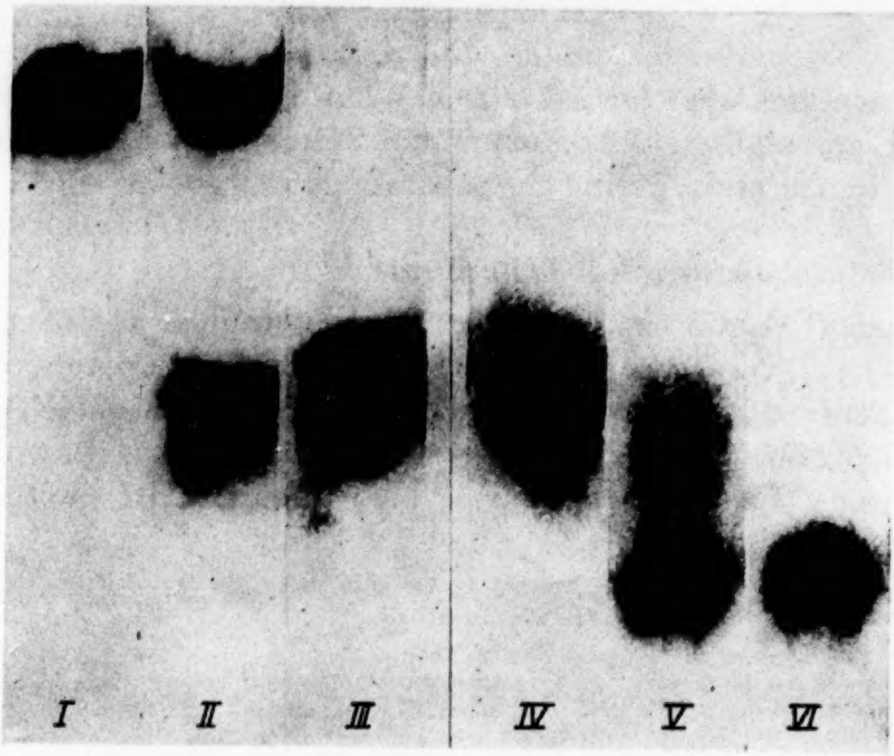

Fig. 2.

Dichlorobis(ethylenediamine)cobalt(III) chloride[3,4,5,6,7]

Analysis for $[Cl_2Co\ en_2]Cl$. Co was determined as $CoSO_4$. Found: *cis* form; Co, 20.54%; *trans* form; 20.67%; calculated: Co, 20.66%.

Solvent mixture: 70 ml of acetone + 20 ml of water + 10 ml of HCl (sp.gr.1.19).

a) Time of separations: 24 hours.

R_F *cis* = 0.52; R_F *trans* = 0.42

b) Time of separations: 40 hours.

R_F *cis* = 0.47 (Fig. 2, IV); R_F *trans* = 0.37 (Fig. 2, VI); mixture of *cis* and *trans*: Fig. 2, V.

On boiling the aqueous solution of *cis*-dinitrobis(ethylenediamine)cobalt(III) nitrate the *cis* isomer is converted to the *trans* form. This conversion is not complete even after 10 hours of boiling. The pure *trans* isomer is obtained by fractional crystallization. Fig. 1 shows the chromatograms of the pure *cis* isomer (IV), *cis* isomer after two hours of boiling (V), after 6 hours of boiling (VI), after 10 hours of boiling (VII) and finally the chromatograms of the pure *trans* isomer (VIII).

SUMMARY

It has been established that *cis* and *trans* stereoisomeric forms of inorganic complex salts can be separated by paper chromatography. In all the cases studied *cis* forms had remarkably greater R_F values than the *trans* ones. It has also been found that the racemic complex compounds can be resolved into their optically active components by paper chromatography by adding an optically active compound to the solvent used in the process of chromatography.

References p. 553.

RÉSUMÉ

On a trouvé qu'il est possible, par la méthode chromatographique sur papier, de séparer les stéréoisomères *cis* des stéréoisomères *trans* de sels complexes inorganiques. Dans tous les cas étudiés les formes *cis* ont des valeurs de R_F plus élevées que les formes *trans*. Dans le cas des racémates de composés complexes, on peut ajouter une substance optiquement active au solvant employé pour la chromatographie.

ZUSAMMENFASSUNG

Es wurde festgestellt, dass man die *cis-trans* Isomere anorganischer komplexer Salze mittels Papierchromatographie trennen kann. In Fällen die man untersucht hat, haben die *cis* Isomeren bedeutend grössere R_F-Werte als *trans* Formen.

Man bemerkt, dass auch die Racemate komplexer Verbindungen in optische Antipoden mittels Papierchromatographie gespalten werden können, falls man in das Lösungsmittel eine optisch aktive Substanz löst.

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ON THE DESALTING OF SOLUTIONS OF AMINO ACIDS BY ION EXCHANGE*

by

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INTRODUCTION

In the chromatographic separation of amino acids by published procedures based on the sodium salt of Dowex 50[1,2], it is frequently convenient to be able to obtain the amino acids in a salt-free form, as for example, in the subsequent checking of the identity of a given constituent by paper chromatography in the experiments of STEIN[3] on urinary amino acids. The specific object of the present study has been a technique for this purpose.

In general, the removal of inorganic ions from amino acid solutions for purposes of paper chromatography has been accomplished either electrolytically, by the procedure of CONSDEN, GORDON AND MARTIN[4],**** or by ion exchange. The use of the latter method has advantages for the purpose of desalting the dilute amino acid solutions encountered in the effluent from Dowex 50, where the salt to amino acid ratio may be 1000 to 1.

The affinities of amino acids for both anion and cation exchangers have been studied in particular detail by PARTRIDGE AND BRIMLEY[7] and have been utilized in a number of procedures for the desalting of amino acid solutions[8,9,10]. In most cases the objective has been to separate a naturally-occurring mixture of amino acids from inorganic salts before application to paper chromatograms. Analysis on Dowex 50[1,3], however, does not require prior desalting of physiological fluids. The column provides directly the separation of the amino acids one from another, and the desalting with which the present study is concerned involves in most instances only a single amino acid dissolved in an excess of buffer. For the neutral and acidic amino acids the desalting has been accomplished by passing the buffered

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** *Chargé de recherche* of the *Fonds National de la Recherche Scientifique*.

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**** In reference to losses of amino acids during electrolytic desalting see STEIN AND MOORE[5] and ROVERY AND DESNUELLE[6].

References p. 558.

mixture over the base form of a strong base resin (Dowex 2), followed by elution with acetic acid. The Na^+ is washed through the resin bed by water, together with the polyoxyethylene lauryl alcohol (BRIJ-35), used as a detergent, and the thiodiglycol used as an antioxidant in the chromatographic experiments[1]. The addition of acetic acid elutes the amino acid and leaves the stronger, non-volatile citric and phosphoric acids of the buffers, as well as chloride ions, on the resin.

The basic amino acids (and tryptophan) are desalted on a sulfonated polystyrene resin (Dowex 50) in the acid form. The anions pass through unretarded. Washing of the bed with $0.5N$ HCl removes Na^+, together with the versene and the benzyl alcohol used in the buffers[1]. The amino acid is eluted with $4N$ HCl.

The amino acids are obtained in the free form or as their hydrochlorides by evaporation of the acetic acid or HCl solutions to dryness. The procedure is designed to give quantitative recoveries of the amino acids. The use of NH_4OH displacement from Dowex 50 has been avoided, since it is known that there are losses of the basic amino acids if alkaline eluants are employed[1].

PROCEDURE

Dowex 2*. A column 0.9 cm in diameter and 2 cm high is prepared in a short chromatograph tube[1,2], using about 0.6 g of moist Dowex 2 in the chloride form which has been cycled with NaOH and HCl to remove impurities which may be present initially. Before use the column is washed with 20 ml of $2N$ NaOH (warmed to about 45°), obtained by diluting a stock solution of 40 per cent. NaOH (CO_2-free) prepared from boiled distilled water. The resin bed should not be left in contact with NaOH any longer than necessary. The rate of flow in the desalting experiments was 20 ml per hour (30 ml per hour per sq.cm cross-sectional area of the column) obtained by the use of air pressure. The column is washed with water until the effluent is neutral. All additions of fluid are made against the wall of the tube, with bent-tip pipets or droppers, to avoid disturbance of the resin bed.

The sample to be desalted was 1 to 4 ml of the $0.1M$ citrate buffers used for the elution of the taurine through phenylalanine group of amino acids from Dowex 50 columns[1] containing 30 to 300 μg or more of amino acid. The pH of the sample is not critical. The limiting factor on a column of the size given is a total load of about 0.8 milliequivalents of Na^+ or corresponding monovalent anion. The solutions should be diluted to about $0.2N$ in Na^+ if the initial buffers exceed this concentration. After the buffer has entered the bed, the resin is washed with 20 ml of water. About 10 ml of $1N$ acetic acid is added. The movement of the acid front down the column can be observed by the change in color of the resin.

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* Strong base exchange resin, Dowex-2 × 8 (200—400 mesh) from Technical Service and Development, The Dow Chemical Co., Midland, Mich., U.S.A.

The amino acid is collected in a fraction starting just before the effluent becomes acid and continuing for 4 ml.

Before re-use, the column is washed with 10 ml of 1N HCl and 5 ml of water, and stored in the chloride form, rather than in the less stable basic form.

Dowex 50*. A 0.9 × 2 cm column is prepared from about 0.9 g of the moist acid form of the resin purified as for chromatography[1]. The bed is washed with 10 ml of 1N HCl and with water until the effluent is neutral. The sample to be desalted, in 1 to 4 ml of the 0.1M phosphate and 0.2M citrate buffers used for tryptophan, histidine, lysine, and arginine elution, was adjusted to a pH below 6 with HCl to reduce the CO_2 content before allowing the sample to flow into the column. Except in the case of arginine, which is very strongly held by Dowex 50, the maximum load under these conditions is about 1.2 milliequivalents of Na^+. The Na^+ is washed through by 20 ml of 0.5N HCl. Tryptophan, lysine and histidine emerge in the first 3 ml after the addition of 4N HCl as eluant. Arginine requires 4 ml.

TABLE I

RECOVERIES OF AMINO ACIDS IN THE DESALTING PROCEDURE

Each amino acid was dissolved in 4 ml of the buffer in which the amino acid emerges in the Dowex-50 × 8 chromatographic procedure[1].

Resin used for desalting	Amino acid	Quantity in µg	Recovery in %
Dowex-50	Arginine	195	103
,,	Histidine	29	98
,,	Lysine	38	100
,,	Tryptophan	88	101
Dowex-2	Glycine	44	99
,,	Alanine	46	98
,,	Valine	52	101
,,	Leucine	35	97.5
,,	Isoleucine	62	95
,,	Serine	118	99
,,	Threonine	84	95
,,	Aspartic acid	85	96
,,	Glutamic acid	109	97
,,	Phenylalanine	86	98
,,	Tyrosine	92	99
,,	Methionine	120	100
,,	Cystine	245	99
,,	Proline	284	99
,,	Taurine	105	102

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* Sulfonated polystyrene resin, Dowex-50 × 8 (200-400 mesh).

RESULTS

To check the quantitativeness of the procedure, experiments were carried out on a fraction collector and 1 ml samples of the acetic acid or HCl effluent were adjusted to pH 5 and analysed by the photometric ninhydrin method[11]. The amino acids were recovered as single peaks centered within the specified 4 ml zones. The recoveries are summarized in Table I. The central 4 ml of each peak always contained at least 90 per cent. of the amino acid, with a 6 ml zone being required to insure 100 per cent. recovery in some experiments.

In the experiments of STEIN[3], the salt-free amino acid solutions were taken to dryness in water-repellent celluloid tubes or vials, the use of which facilitates solution of the residue in 0.1 ml of water for transfer of 10 μl quantities containing 2 to 10 μg of amino acid to paper chromatograms. Silicone-treated glass tubes[12] might similarly be used.

DISCUSSION

For larger than 4 ml samples of the specified buffers, or for buffers of higher molarity, there should be a proportional increase in the cross-sectional area of the ion exchange bed used. In practice, it is possible to observe whether the limit of capacity of a given Dowex 2 column is being approached by noting how far down the bed the change of resin color proceeds during the addition of the sample to be desalted. The salt in the sample should not cause more than half of the bed to be converted to the lighter neutral form.

The procedures can be scaled up for the isolation of larger amounts of salt-free amino acids from Dowex 50 chromatograms. Such a need can arise in isotopic tracer experiments with amino acid mixtures, or in the isolation of unknown amino acids from the effluent, as, for example, in the characterization of 3-methylhistidine by TALLAN *et al.*[13]

If the mixture to be desalted contains all of the common amino acids, the following limitations apply to the above conditions: Dowex 2 does not hold arginine and there may be only partial retention of lysine. Histidine is satisfactorily desalted. Glucosamine is recovered in 80 per cent. yield. Tryptophan recovery is only about 50 per cent. from the Dowex 2 bed. If required, Dowex 50 could be used to recover arginine and lysine from the forefraction in the Dowex 2 experiment.

SUMMARY

The removal of sodium citrate and phosphate buffers from amino acids in the effluent from ion exchange chromatograms can be accomplished by one-step desalting on basic or acidic resins. At "salt/amino acid" ratios of 1000 to 1, the amino acid recovery is quantitative. The neutral and acidic amino acids are adsorbed on a strong base resin (Dowex 2) and eluted with acetic acid. The basic amino acids and tryptophan are adsorbed on an acid resin (Dowex 50) and eluted with HCl. The resulting salt-free solutions are suitable for examination by paper chromatography or for the isolation of amino acids for further characterization.

References p. 558.

RÉSUMÉ

L'élimination des tampons au citrate ou au phosphate de sodium des solutions d'acides aminés, obtenues par séparation chromatographique sur échangeurs d'ions, peut être réalisée en une seule opération sur résines basiques ou acides. Quand le rapport „sel/acide aminé" correspond à 1.000 pour 1, la récupération de l'acide aminé est quantitative. Les amino-acides neutres et acides sont adsorbés sur une résine fortement basique (Dowex 2) et élués au moyen d'acide acétique. Les amino acides basiques et le tryptophane sont adsorbés sur une résine acide (Dowex 50) et élués par HCl. Les solutions obtenues, dépourvues de sels, conviennent pour la chromatographie sur papier ou pour l'isolement des acides aminés en vue d'une caractérisation plus approfondie.

ZUSAMMENFASSUNG

Die Elimination von Citrat- oder Phosphatpuffern aus Lösungen von Aminosäuren, welche durch Chromatographie mit Ionenaustauschern gewonnen wurden, kann in einer einzigen Operation mittels basischen und sauren Harzen vorgenommen werden. Wenn das Verhältnis Salz/Aminosäure 1000 zu 1 entspricht, ist die Wiedergewinnung der Aminosäure quantitativ. Die neutralen und die sauren Aminosäuren werden auf einem stark basischen Harz (Dowex 2) adsorbiert und mit Essigsäure eluiert. Die basischen Aminosäuren und das Tryptophan werden auf einem sauren Harz (Dowex 50) adsorbiert und mit HCl eluiert. Die so erhaltenen Lösungen, die nun von Salzen befreit sind, können der Papierchromatographie unterzogen werden oder zur Isolierung der Aminosäuren verwendet werden im Hinblick auf eine genauere Charakterisierung.

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SPECTROPHOTOMETRIC METHOD FOR THE ESTIMATION OF AMINO ACIDS WITH SENSITIZED SCHIFF'S REAGENT

by

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Schiff's reagent has previously been used [1,2] for the detection and determination of aldehydes. TOBIE[3] extended its use to test for free aldehydic groups in simple aldoses, after sensitizing it with the minimum content of SO_2. This sensitized Schiff's reagent has recently been employed by the author[4] for a quantitative determination of ammonium acetate in solution, and also for the determination of the relative strength of organic acids.

The present paper is an extension of its use for the determination of amino acids in solution. The underlying principle is the fact that the basic groups of amino acids are capable of reacting with SO_2, which is present partly free and partly in a loose combination with fuchsin molecules in Schiff's reagent[5]. As the SO_2 is used up, the colour of free fuchsin molecules is developed. If the reaction is quantitative, the intensity of colour should give a measure of the content as well as the dissociation of amino acids. The author is not aware of any previous use of Schiff's reagent for the determination of amino acids in the manner described above.

EXPERIMENTAL

A B.D.H. sample of fuchsin was crystallized before use. Samples of amino acids are those of Merck's.

Schiff's reagent was prepared according to TOBIE[3]'s method. 0.5 g of fuchsin was decolourized by adding the calculated amount of H_2SO_3 so as to maintain 1 g of SO_2 per litre, and the volume then made up to 1000 ml. The solution after standing overnight showed a light yellow colour which was removed by treatment with minimum quantity of activated charcoal. Following the above procedure two sets of reagents were prepared, one containing 1 g of SO_2/litre and the other 2 g of SO_2/litre.

All spectrophotometric measurements were carried out with Beckman's Spectrophotometer (Model D-U) at a slit width of 0.04 mm. Preliminary analysis of the coloured compounds, obtained with sensitized Schiff's reagent and any of the amino acids, such as, glycine, alanine, norvaline, leucine and methionine, showed that in every case the absorption maxima of the coloured compounds occurred at the characteristic wavelength, 535 mμ of fuchsin itself. All measurements have, therefore, been made at this wavelength.

In order to draw a standard curve of optical density against concentration of amino acids, the following procedure was adopted.

5 ml of sensitized Schiff's reagent (1 g SO_2/litre) are transferred to several test tubes in series. Different quantities ranging from 0.005 to 0.1 g of a particular amino acid are added in the test tubes, keeping a regular time interval between two consecutive additions. The colour is allowed to develop and optical densities are recorded in every case 15 min (chosen arbitrarily) after mixing the reagents. Following the same procedure, under identical conditions, the optical densities against concentration curves of glycine, alanine, norvaline, leucine and methionine were also drawn. In order to observe the effect of increasing the SO_2 content on the sensitivity of the colour development, glycine was added to a Schiff's reagent containing 2 g instead of 1 g SO_2/litre. The curves are presented in Fig. 1.

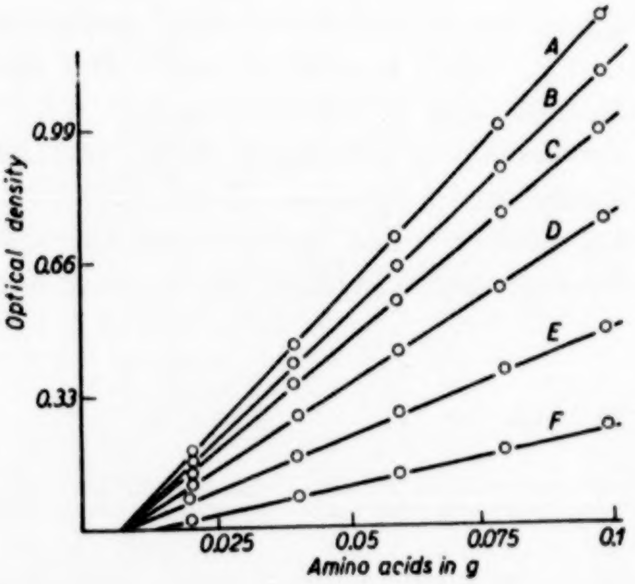

Fig. 1

Curve A — Glycine
with Schiff's (1 g SO_2/litre)
Curve B — Alanine ,,
Curve C — Norvaline ,,
Curve D — Leucine ,,
Curve E — Methionine ,,
Curve F — Glycine
with Schiff's (2 g SO_2/litre)

With the object of checking the reproducibility of the graphs and hence of the measurements, different solutions of the amino acids were randomly examined by the above procedure for their optical densities. The concentrations were then measured from the calibration curves. Table I gives an idea of the accuracy of the method. The results are well within 1% of the theoretical quantities. In Table II are shown the slopes of the straight line graphs of the amino acids used and the respective R_F values obtained by paper chromatography. The inverse relationship is quite obvious.

References p. 562.

RESULTS

TABLE I

AMOUNT OF AMINO ACIDS IN g, A′ THEORETICAL AND B′ EXPERIMENTAL (FOUND BY THE PROPOSED METHOD)

	Glycine	Alanine	Norvaline	Leucine	Methionine
A′	0.033	0.042	0.037	0.028	0.025
B′	0.0325	0.042	0.0365	0.028	0.025
A′	0.049	0.069	0.054	0.044	0.037
B′	0.049	0.068	0.054	0.045	0.037
A′	0.0715	0.081	0.069	0.068	0.077
B′	0.072	0.082	0.070	0.0675	0.078

TABLE II

SLOPES OF OPTICAL DENSITY AGAINST CONCENTRATION CURVES PER 0.02 g OF AMINO ACIDS AND R_F VALUES

	Glycine	Alanine	Norvaline	Leucine	Methionine
R_F	0.42	0.58	0.79	0.82	0.79
R_F	—	—	0.48	—	0.57
Slopes	0.267	0.237	0.206	0.160	0.104

R_F values have been taken from the work of BURMA[6]; phenol water and S-collidine water were taken as the developing solution.

DISCUSSION

The effect of the SO_2 content of Schiff's reagent is at once clear from the curve A and F. For instance, an increase in SO_2 content greatly reduces the sensitivity of the reagent. Again, there is a need for a minimum SO_2 content in the reagent in order to keep the dye in the leuco state. It is for this reason that a certain quantity of free SO_2 must be present in the reagent, consequently the colour is not developed until the free SO_2 is consumed by the added amino acid. This free SO_2 content, therefore, decides the lower limit of amino acid that can be estimated by the proposed manner. There appears to be no upper limit as in the case of the determination of ammonium acetate[4].

The neutralization of SO_2 molecules bound up loosely to fuchsin, as in Schiff's reagent, by the amino acids probably depends upon the ionization of the respective acids. The greater the ionization the higher the solubility is likely to be, which, according to the fundamental equation of chromatography, is inversely proportional to their R_F values. The inverse relation between slopes and R_F values as given in Table II is obvious. The present method of determining amino acids (not in a mixture) is easy and quick to manipulate and compares well in accuracy with the other photometric methods, for example those described by DANIELSON[7].

ACKNOWLEDGEMENT

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SUMMARY

A spectrophotometric method for the estimation of amino acids with a sensitized Schiff's reagent has been described.

1. Amino acids such as glycine, alanine, norvaline, leucine and methionine use up the SO_2 bound to the fuchsin molecule in Schiff's reagent and thus the colour is developed.
2. The intensity of colour depends upon the quantity of the amino acid as well as its nature.
3. The sensitivity of the reaction is decreased by increasing the SO_2 content of the reagent.
4. The slopes of the optical density against concentration curves appear to be characteristic of the amino acids; for example they are inversely proportional to the R_F values.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage des acides aminés avec le réactif de Schiff sensibilisé.

1. Des acides aminés tels que la glycine, l'alanine, la norvaline, la leucine et la méthionine colorent le réactif de Schiff.
2. L'intensité de la coloration dépend de la teneur en acide aminé et de la nature de cet acide.
3. La sensibilité de la réaction diminue avec l'augmentation de la teneur en SO_2 du réactif.
4. Les pentes obtenues pour la densité optique en fonction des concentrations paraissent être caractéristiques de chaque acide aminé; elles sont, par exemple, inversément proportionnelles aux valeurs de R_F obtenues par chromatographie sur papier.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben für die spektrophotometrische Bestimmung von Aminosäuren mit sensibilisiertem Schiff'schen Reaktiv.

1. Aminosäuren, wie Glycin, Alanin, Norvalin, Leucin und Methionin färben das Schiff'sche Reaktiv.
2. Die Intensität der Färbung hängt vom Gehalt an Aminosäure und von deren Natur ab.
3. Die Sensibilität der Reaktion wird vermindert mit Erhöhung des Gehaltes an SO_2 des Reaktives.
4. Es scheint, dass die Kurven der optischen Dichte in Funktion der Konzentrationen charakteristisch sind für die einzelnen Aminosäuren. Sie sind z.B. umgekehrt proportional den R_F-Werten, die durch Papierchromatographie erhalten werden.

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THE USE OF CHROMIUM METAL AS INDICATOR ELECTRODE IN ELECTROMETRIC TITRATIONS

by

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Several metal electrodes including tungsten[1], antimony[2], tellurium[3], molybdenum[4], and arsenic[5] satisfy the condition of functioning as metal-metal oxide[6] or metal-metal oxide-oxygen electrodes[7] and can thus be applied as indicator electrodes in acid-base titrations. Stick chromium electrodes prepared by the mechanical shaping of the pure massive metal can be used satisfactorily for the same purpose. The high passivity of the metal contributes to its considerable inertness and apparently does not affect the permeability of its surface to electrons and thus provides the metal with the additional advantage that it can function also as an indicator electrode in redox titrations.

EXPERIMENTAL

The solutions. For the potential measurements the CLARK AND LUBS series of buffers[8] (pH 1—10), the Ringer buffers[9] (pH 11—12) and the Universal buffer mixture of BRITTON AND ROBINSON[10] were used. These were checked for their pH values using the hydrogen electrode. The acids titrated included hydrochloric, nitric, acetic, boric, sulphuric, oxalic, malonic, succinic, tartaric, maleic, citric and phosphoric acids. The solutions were prepared from chemically pure materials and standardized with a carbonate-free sodium hydroxide solution prestandardized against potassium hydrogen phthalate.

The materials used in the oxidation-reduction titrations included potassium permanganate, potassium dichromate, vanadyl chloride, ferrous ammonium sulphate, thallous acetate, sodium tellurite, sodium thiosulphate, uranous sulphate and titanous chloride solutions. Chemically pure products were used for preparing the solutions which were standardized according to recommended procedures [11-16].

The titration device and the working procedure were the same as previously described[17]. All potential measurements were performed at a constant temperature in an air or water thermostat at 30° C ± 0.05%.

RESULTS

The acid-base titrations.

The time-potential and pH-potential curves. As may be seen from the curves shown in Fig. 1 the potentials set up by the massive chromium electrode after equilibrium has been attained manifest only very slight variations with time over a period of two hours. This indicates that drifts in potential during a titration are not liable to occur. The period required for the initial equilibrium to be attained before any set of titrations amounts maximally to one hour. It is, therefore, desirable before performing a series of successive titrations to bathe the refreshed electrode in a buffer solution for that period of time.

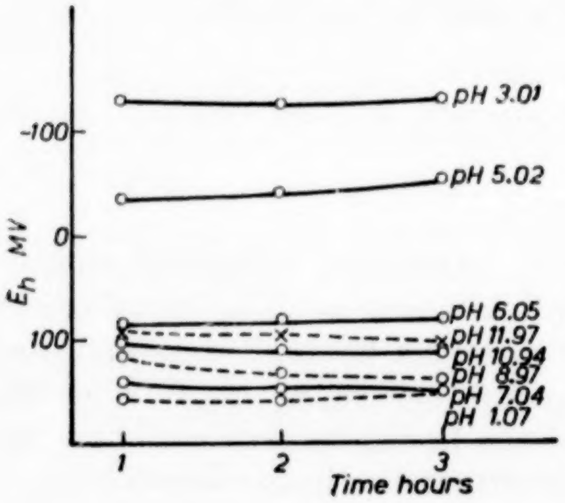

Fig. 1.

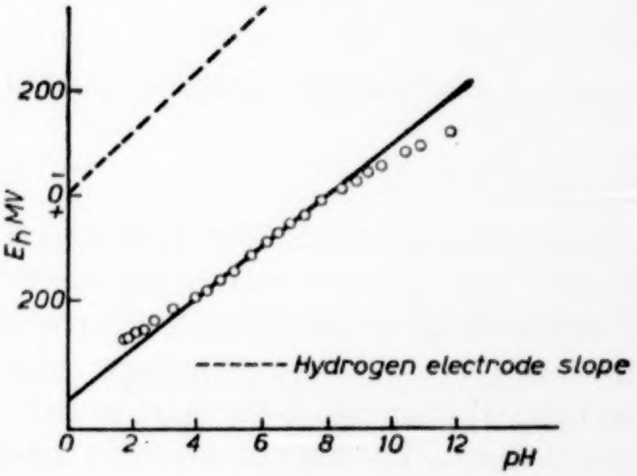

Fig. 2.

In constructing a calibration curve for the chromium electrode, 50 ml portions of the universal buffer mixture were titrated with 0.2N carbonate-free sodium hydroxide solution using two electrodes of the same dimensions (each 1 cm in length and 7 mm in diameter). Both electrodes gave practically identical values, manifesting thus considerable reproducibility. The pH-potential curve as represented by Fig. 2 indicates regular variation of potential with pH from 3 to 10 with $\triangle E/\triangle pH$ amounting to 48.5 mv per unit pH.

From the neutralization curves of the aforementioned acids, some of which are shown in Figs. 3 and 4, the following conclusions can be drawn:

a. The titration curves of the monobasic acids are characterized by sharp inflections in the region of the end-points varying from 150 to 250 mv. Boric acid yields, however, a very poor inflection, unless glycerol is present, in which case the inflection amounts to 100 mv.

b. The titration curves of the dibasic acids manifest two inflections the first of which, except in the case of maleic, is not sharp enough to permit the detection of the inflection point. The second inflections are sharp and amount to 80-150 mv.

c. Phosphoric acid gives two inflections corresponding to the first and second

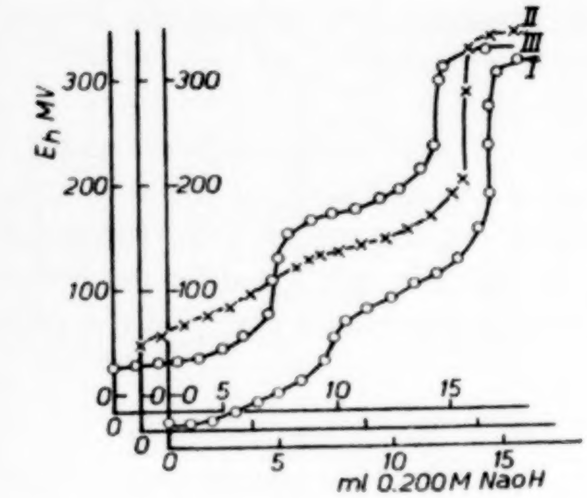

Fig. 3.

I 15 ml 0.0977M oxalic acid
II 15 ml 0.0985M succinic acid
III 15 ml 0.0983M maleic acid

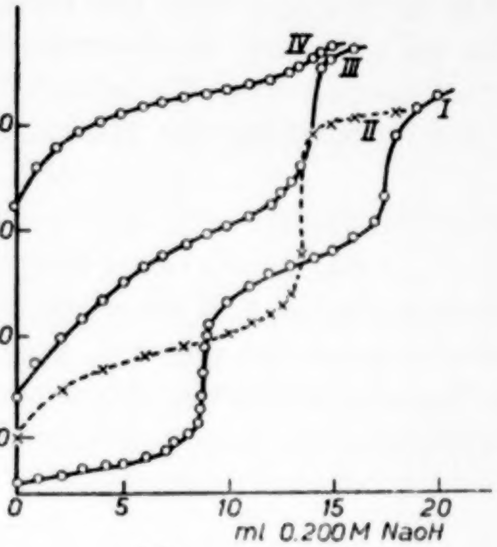

Fig. 4.

I 15 ml 0.1185M phosphoric acid
II 25 ml 0.1089M acetic acid
III 25 ml 0.1112M boric acid + glycerol
IV 25 ml 0.1112M boric acid alone

steps of neutralization, whereas citric acid shows but a single inflection corresponding to the third step.

In all the above cases the end-points computed from the titration curves coincide practically with those obtained by the use of suitable indicators as is shown in Table I.

TABLE I

Acid	HCl	HNO_3	Boric	Acetic	H_2SO_4	Oxalic	Malonic
End-point by indicator	14.00	13.35	13.90	13.60	13.65	14.65	16.04
Observed end-point	14.05	13.38	13.88	13.60	13.68	14.63	16.04
Error %	+ 0.36	+ 0.22	— 0.14	0.00	+ 0.22	— 0.14	0.00

Acid	Succinic	Tartaric	Maleic		Phosphoric		Citric
			1st step	2nd step	1st step	2nd step	
End-point by indicator	14.78	14.78	7.37	14.74	8.81	17.62	15.46
Observed end-point	14.76	14.82	7.39	14.76	8.83	17.62	15.51
Error %	— 0.13	+ 0.27	+ 0.27	+ 0.13	+ 0.23	0.00	+ 0.32

Although massive chromium can be used satisfactorily as an indicator electrode in acid-base titrations, it cannot be used with certainty for the direct determination of pH unless previously calibrated. This can be deduced from the fact that $\Delta E/\Delta pH$

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(Fig. 2) deviates from the theoretical values by ∿ 12 mv, and further because the pK'_a values, as determined from the neutralization curves of the weaker acids, deviate from the reported values by amounts exceeding permissible errors. Thus by applying the HENDERSON-HASSELBALCH equation[18]

$$\text{pH} = \text{p}K'_a + \log\,[\text{Salt}]/[\text{Acid}],$$

in which [Salt] = % acid neutralized, [Acid] = % acid unneutralized and pH $= (E_0' - E_h)/X$; E_h being the potential set when 40, 50 and 60% of the acid have been neutralized, X the slope of the E_h—pH curve (Fig. 2) and E'_0 the intercept on the E axis at pH = 0, and by taking $E'_0 = 393$ mv, pK'_a values, as listed in Table II, are obtained which show deviations varying between 0.12 and 1.2 pK_a units from the reported values.

TABLE II

Acid	Acetic	Boric	Oxalic 1st step	Oxalic 2nd step	Malonic 1st step	Malonic 2nd step	Succinic 1st	Succinic 2nd
pK'_a found	4.82	9.62	2.74	5.09	3.82	6.29	4.74	6.04
pK_a reported	4.70[19]	9.20[20]	2.00[20]	4.39[21]	2.84[22]	5.66[22]	4.00[20]	5.59[22]

Acid	Tartaric 1st	Tartaric 2nd	Maleic 1st	Maleic 2nd	Phosphoric 1st	Phosphoric 2nd	Citric 3rd
pK'_a found	4.25	5.33	3.13	6.64	2.67	6.62	6.84
pK_a reported	3.05[23]	4.39[21]	1.93[21]	6.60[24]	2.03[20]	6.80[25]	5.80[20]

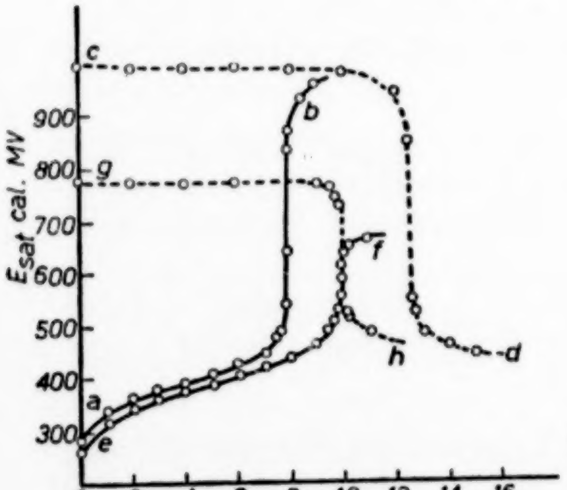

Fig. 5.

(a—b) 10 ml 0.0995N Fe^{+2} × 0.1261N MnO_4^-
(c—d) 10 ml 0.1261N MnO_4^- × 0.0995N Fe^{+2}
(e—f) 10 ml 0.0995N Fe^{+2} × 0.0993N $Cr_2O_7^{-2}$
(g—h) 10 ml 0.0993N $Cr_2O_7^{-2}$ × 0.0995N Fe^{+2}

The oxidation reduction reactions

Table III and the corresponding curves (Figs. 5 and 6) show a series of redox reactions that can be carried out in the presence of the massive chromium electrode.

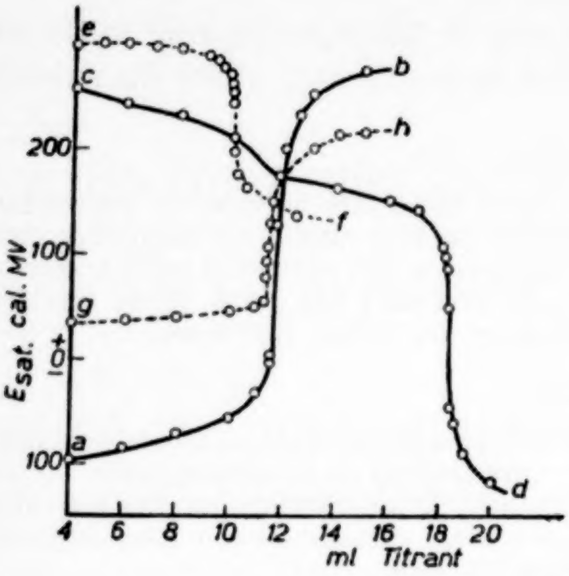

Fig. 6.
(a—b) 10 ml 0.088N Tl^+ × 0.1261N MnO_4^-
(c—d) 10 ml 0.0909N MnO_4^- × 0.0296N V^{+4}
(e—f) 10 ml 0.1001N($Cr_2O_7^{-2}$+I^-) × 0.099N $S_2O_3^{-2}$
(g—h) 10 ml 0.0793N Te^{+4} × 0.1163N MnO_4^-

TABLE III

Titration system	Inflection with Pt per 0.1 ml of titrant	Inflection with Cr per 0.1 ml of titrant	Theoretical end-point	End-point with Pt	End-point with Cr
Acid Reactions	mv			ml	
Fe^{+2} in 2N H_2SO_4 with MnO_4^-	430	390	7.89	7.88	7.87
MnO_4^- in 5N H_2SO_4 with Fe^{+2}	425	296	12.67	12.55	12.53
Fe^{+2} in 2N HCl with $Cr_2O_7^{-2}$	80	60	10.00	—	9.98
$Cr_2O_7^{-2}$ in 2N HCl with Fe^{+2}	330	180	9.98	9.96	9.97
I_2 with $S^2O_3^{-2}$	80	60	10.04	10.02	10.02
U^{+4} in 2N H_2SO_4 with MnO_4^-	660	560	7.73	7.76	7.79
U^{+4} in 1N HCl with $Cr_2O_7^{-2}$	280	290	21.55	21.53	21.55
Ti^{+3} in 2N HCl with $Cr_2O_7^{-2}$	160	160	10.35	10.35	10.35
Alkaline Reactions					
MnO^-_4 in 0.5N NaOH with V^{+4}	100	80	18.42	18.33	18.33
Tl^+ in 0.1N NaOH with MnO^-_4	134	127	11.63	11.67	11.65
Te^{+4} in 0.1N NaOH with MnO^-_4	175	50	11.36	11.37	11.34

The representative results depicted in the above table reveal that the inflections at the end-points, although mostly smaller than those obtained in the presence of the platinum electrode, possess in many cases considerable magnitude. They coincide practically with the theoretical values and with those obtained with the platinum electrode. They indicate further the reliability of the chromium electrode for use, not only in alkaline, but also in fairly strong acid media and in conjunction with strong reducing agents that do not seem to affect the passivity of the electrode.

SUMMARY

Massive chromium because of the passivity of the oxide formed on its surface, can be used as a substitute for platinum in electrometric titrations including acid-base and oxidation-reduction systems. The end-points are attended with comparatively large jumps on the curves and compare satisfactorily with those obtained using the hydrogen or the platinum electrode or by other methods.

RÉSUMÉ

Le chrome, grâce à l'inertie de son oxyde se formant en surface, peut être utilisé à la place du platine dans les titrations électrométriques de systèmes acide — base et oxydo-réducteur. Les points finaux sont donnés sur les courbes par des inflexions relativement larges; ils peuvent être comparés à ceux obtenus avec une électrode à hydrogène ou de platine, ou par d'autres méthodes.

ZUSAMMENFASSUNG

Festes Chrom kann, dank der passivierenden Oxydschicht an seiner Oberfläche als Ersatz für Platin in elektrometrischen Titrationen, seien diese Saüre-Basen oder Redox Titrationen, verwendet werden. Die Endpunkte sind von verhältnissmässig grossen Sprüngen begleitet und sind gut vergleichbar mit denjenigen, die mit der Wasserstoff, der Platin-Elektrode oder mit anderen Methoden erhältlich sind.

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POTENTIOMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS

XIX. OXIDATION WITH CHLORAMINE-B

by

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AFANAS'EV[1] reported that chloramine-B is a good substitute for chloramine-T in analytical chemistry. B. SINGH AND G. SINGH[2] used chloramine-B as an oxidizing agent to determine indirectly potassium iodate, potassium metaperiodate, potassium bromate, potassium dichromate, hydrogen peroxide, chloramine-T and potassium permanganate by a potentiometric method.

In the present investigation chloramine-B has been used as an oxidizing agent for the potentiometric determination of potassium ferrocyanide, hydroquinone, hydrazine sulphate, potassium antimonyl tartrate, ferrous sulphate, quinhydrone, potassium iodide and arsenious oxide. In acid medium these substances react with chloramine-B according to the following equations:

$$C_6H_5SO_2N(Na)Cl + 2K_4[Fe(CN)_6] + 2HCl = C_6H_5SO_2NH_2 + NaCl + 2K_3[Fe(CN)_6] + 2KCl.$$

$$C_6H_5SO_2N(Na)Cl + C_6H_4(OH)_2 = C_6H_5SO_2NH_2 + NaCl + C_6H_4O_2.$$

$$2C_6H_5SO_2N(Na)Cl + N_2H_4 = 2C_6H_5SO_2NH_2 + 2NaCl + N_2$$

$$2C_6H_5SO_2N(Na)Cl + 2KSbO.C_4H_4O_6 + 3H_2O = 2C_6H_5SO_2NH_2 + 2NaCl + Sb_2O_5 + 2KHC_4H_4O_6.$$

$$C_6H_5SO_2N(Na)Cl + 2FeSO_4 + H_2SO_4 = C_6H_5SO_2NH_2 + NaCl + Fe_2(SO_4)_3$$

$$C_6H_5SO_2N(Na)Cl + C_6H_4O_2.C_6H_4(OH)_2 = C_6H_5SO_2NH_2 + NaCl + 2C_6H_4O_2$$

$$C_6H_5SO_2N(Na)Cl + 2HI = C_6H_5SO_2NH_2 + NaCl + I_2$$

$$2C_6H_5SO_2N(Na)Cl + As_2O_3 + 2H_2O = 2C_6H_5SO_2NH_2 + 2NaCl + As_2O_5.$$

EXPERIMENTAL

A known weight of each substance was mixed with dilute acid and titrated against standard chloramine-B solution by a potentiometric method. The mixture was kept stirred by a mechanical stirrer during the titrations. A bright platinum foil immersed in the solution to be titrated was used as an oxidation-reduction electrode, and this was coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge. The cell was placed in a water bath at 25° C.

During the titration the progress of the reaction was studied potentiometrically. At the equivalence point a sharp jump in potential was observed in each titration.

A series of potentiometric titrations were performed with different amounts of each substance. One titration, as typical of the set, is recorded in Table I.

TABLE I

TITRATION OF 0.2955 g OF POTASSIUM FERROCYANIDE MIXED WITH 10 ml OF WATER AND 10 ml OF $N/2$ HCl, AGAINST 0.049M CHLORAMINE-B.

Chloramine-B ml	E.M.F. (volts)	E/C. (m volts/ml)	Chloramine-B ml	E.M.F. (volts)	E/C. (m volts/ml)
0.00	0.1498				1504 (Max.)
1.00	0.2197	70	7.15	0.4973	1080
2.00	0.2765	57	7.20	0.5513	161
3.00	0.2919	15	7.50	0.5996	99
4.00	0.3037	12	8.00	0.6489	40
5.00	0.3150	11	9.00	0.6891	32
6.00	0.3287	14	10.00	0.7213	10
6.50	0.3498	42	11.00	0.7310	7
7.00	0.3843	69	12.00	0.7378	2
7.05	0.3979	272	13.00	0.7401	2
7.10	0.4221	484	14.00	0.7419	

The titrations, one for each substance, are represented by the curves, A to H, given in the Fig. 1.

In these titrations it is evident that with the addition of the titrant the E.M.F. rose steadily till the equivalence point. At the equivalence point there was a sharp jump in potential followed by a steady rise.

From the amount of chloramine-B used, corresponding to the equivalence point in each titration, the amount of each substance was calculated. The results given in Tables II to IX show that these substances can be determined by a potentiometric method, using chloramine-B as an oxidizing agent.

TABLE II

POTASSIUM FERROCYANIDE

$K_4[Fe(CN)_6]\cdot 3H_2O$ taken g	Chloramine-B used g	$K_4[Fe(CN)_6]\cdot 3H_2O$ found g
0.2955	0.0936	0.2953
0.4224	0.1339	0.4227
0.6335	0.2008	0.6337
0.9293	0.2944	0.9292
1.1404	0.3609	1.1400

References p. 573.

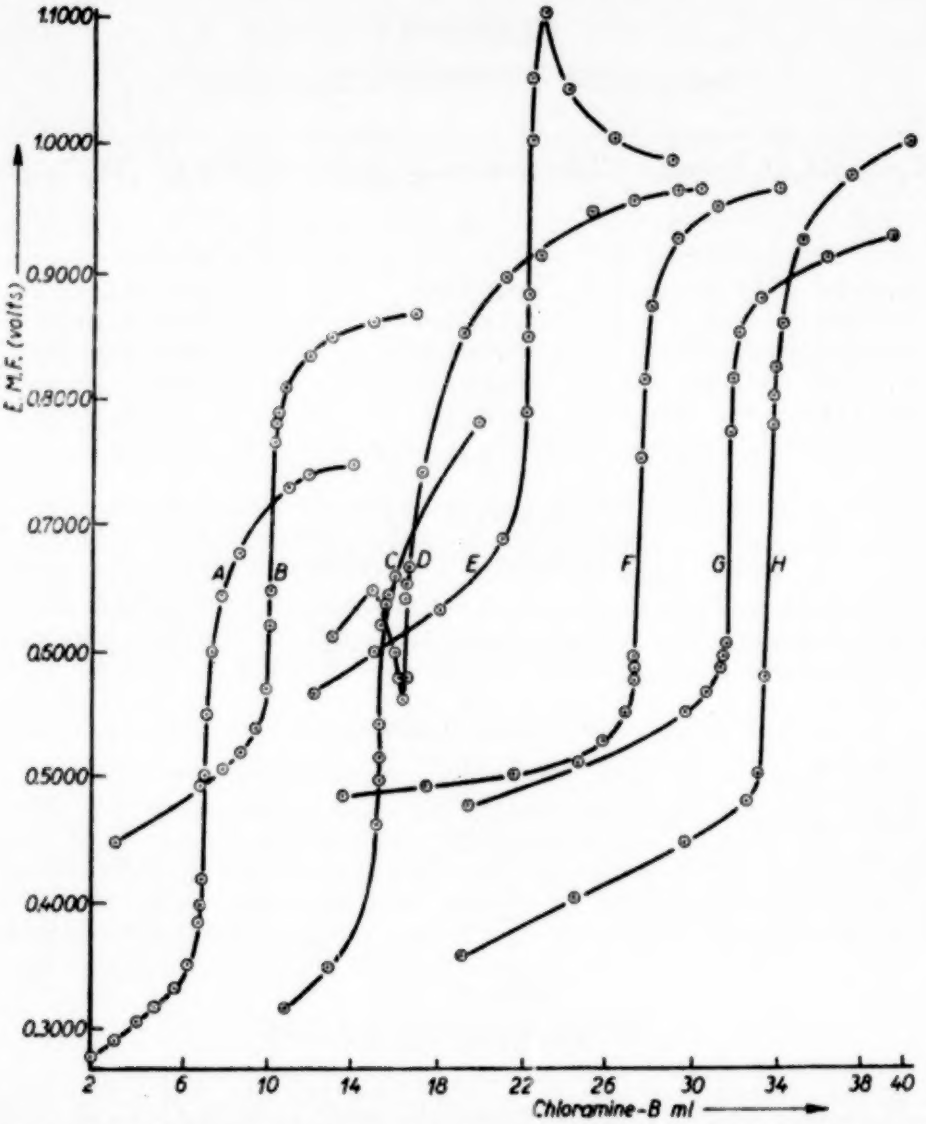

Fig. 1. Curves A-H refer respectively to $K_4[Fe(CN)_6].3H_2O$, $C_6H_4(OH)_2$, $N_2H_4 \cdot H_2SO_4$, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, $FeSO_4 \cdot 7H_2O$, $C_6H_4O_2.C_6H_4(OH_2)$, KI and As_2O_3.

TABLE III

HYDROQUINONE

$C_6H_4(OH)_2$ taken g	Chloramine-B used g	$C_6H_4(OH)_2$ found g
0.0550	0.1339	0.0550
0.0825	0.2007	0.0826
0.1211	0.2941	0.1209
0.1487	0.3610	0.1486
0.1818	0.4413	0.1817

TABLE IV

HYDRAZINE SULPHATE

$N_2H_4.H_2SO_4$ taken g	Chloramine-B used g	$N_2H_4.H_2SO_4$ found g
0.0325	0.1338	0.0325
0.0480	0.2007	0.0480
0.0715	0.2940	0.0714
0.0878	0.3610	0.0877
0.1073	0.4416	0.1073

References p. 573.

TABLE V

POTASSIUM ANTIMONYL TARTRATE

$K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$ taken g	Chloramine-B used g	$K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$ found g
0.1670	0.1339	0.1671
0.2673	0.2140	0.2670
0.3674	0.2942	0.3672
0.4509	0.3613	0.4507
0.5511	0.4416	0.5509

TABLE VI

FERROUS SULPHATE

$FeSO_4 \cdot 7H_2O$ taken g	Chloramine-B used g	$FeSO_4 \cdot 7H_2O$ found g
0.2780	0.1338	0.2782
0.4170	0.2007	0.4170
0.6116	0.2941	0.6112
0.7506	0.3609	0.7503
0.9174	0.4412	0.9170

TABLE VII

QUINHYDRONE

$C_6H_4O_2 \cdot C_6H_4(OH)_2$ taken g	Chloramine-B used g	$C_6H_4O_2 \cdot C_6H_4(OH)_2$ found g
0.1090	0.1339	0.1091
0.1635	0.2007	0.1636
0.2398	0.2942	0.2397
0.2943	0.3610	0.2943
0.3597	0.4412	0.3596

TABLE VIII

POTASSIUM IODIDE

KI taken g	Chloramine-B used g	KI found g
0.1660	0.1338	0.1661
0.2490	0.2008	0.2491
0.3652	0.2943	0.3652
0.4482	0.3613	0.4484
0.5478	0.4415	0.5479

References p. 573.

TABLE IX

ARSENIOUS OXIDE

As_2O_3 taken g	Chloramine-B used g	As_2O_3 found g
0.0495	0.1338	0.0495
0.0742	0.2007	0.0743
0.1088	0.2941	0.1088
0.1335	0.3610	0.1337
0.1632	0.4412	0.1633

SUMMARY

Chloramine-B has been used as an oxidizing agent to determine potassium ferrocyanide, hydroquinone, hydrazine sulphate, potassium antimonyl tartrate, ferrous sulphate, quinhydrone, potassium iodide and arsenious oxide by a potentiometric method. In acid medium each substance is titrated with a standard solution of chloramine-B, using platinum foil as an oxidation-reduction electrode coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge.

RÉSUMÉ

La chloramine-B est proposée comme oxydant pour le dosage potentiométrique du ferrocyanure de potassium, de l'hydroquinone, du sulfate d'hydrazine, du tartrate d'antimonyle et de potassium, du sulfate de fer(II), de la quinhydrone, de l'iodure de potassium et de l'anhydride arsénieux. En milieu acide, chaque substance est titrée avec une solution étalon de chloramine-B, au moyen d'une électrode d'oxydo-réduction en platine et d'une électrode de calomel saturée, reliées par un pont agar-agar — chlorure de potassium.

ZUSAMMENFASSUNG

Das Chloramin-B wird als Oxydationsmittel vorgeschlagen für die potentiometrische Bestimmung von Kaliumferrocyanid, Hydrochinon, Hydrazinsulfat, Kalium- und Antimonyltartrat, Eisen(II)sulfat, Chinhydron, Kaliumjodid, arsenige Säure. In saurem Milieu wird jede Substanz mit einer Lösung von Chloramin-B titriert mit Hilfe einer Ox/Red-Elektrode aus Platin und einer gesättigten Kalomelelektrode, welche durch eine Brücke aus Agar-Agar/Kaliumchlorid verbunden sind.

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COULOMETRIC AND POLAROGRAPHIC DETERMINATIONS OF TRACE AMOUNTS OF LEAD

by

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The desirability of a method for the measurement of small amounts of lead where the analyst could be completely isolated from the sample prompted the investigation of the use of a small mercury-plated platinum electrode. In order to compete with the more cumbersome dithizone extraction, the proposed method would have to be applicable for the determination of lead in 1-100 μg amounts in aqueous solution at concentrations of the order of $1 \cdot 10^{-6} M$. The mercury-plated platinum electrode which had previously been used in unstirred solutions in this laboratory gave reliable results with cadmium, when used polarographically[9] to a concentration of $1 \cdot 10^{-4} M$, and coulometrically to $1 \cdot 10^{-5} M$[3]. From the work of ARTHUR *et al*[1]. it was apparent that a large increase in sensitivity could be achieved by uniform stirring of the solution. COOKE[2] has already shown that one can obtain a similar increase in sensitivity by rotating an amalgam electrode in the same way as platinum or by using a large pool[10]. Most recently, KOLTHOFF AND JORDAN[6] have reported briefly on the combined use of stirring the solution and counter-current rotation of the electrode to achieve currents which are no longer diffusion-controlled.

Another attack upon the instrumental measurement of small amounts of lead has been the high sensitivity polarograph reported by KELLEY AND MILLER[5]. However, their work did not appear to have the desired precision, while COOKE on the rotating amalgam electrode gave no estimation of precision or accuracy. It was thus decided that the stationary mercury electrode when used in a stirred solution had much to offer since it could be used either polarographically or coulometrically. Furthermore, since the coulometric technique could be used without rigorous exclusion of oxygen, it was expected that high precision could be obtained for very dilute concentrations of lead with a minimum of precautions.

APPARATUS AND PROCEDURES

The electrolysis cell pictured in Fig. 1 was so constructed, that a small mercury-plated platinum electrode seated in a fixed glass tube, could be placed inside of a glass tube which was rotated at 600 r.p.m. By stirring the solution about the electrode in this manner a significant increase in the deposition current could be obtained. Coulometric and polarographic measurements could also be made with the electrode while a steady stream of prepurified nitrogen was forced into the cell, since the outer glass tubing prevented nitrogen bubbles from coming into contact with the electrode. The cell permitted 100 ml of solution to be removed without change in the position of the electrode with respect to the stirring tube and would be readily adaptable for continuous measurements on flowing systems.

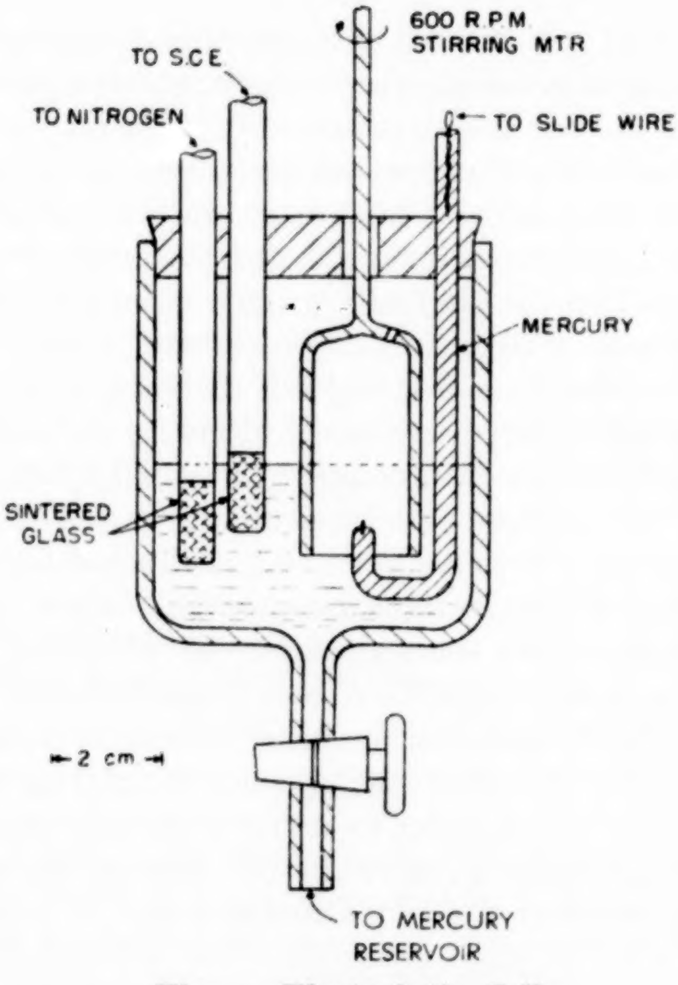

Fig. 1. Electrolytic Cell.

The current-voltage curves were obtained in the conventional manner, except that for the coulometric studies the rate of polarization of the electrode had to be significantly faster than the usual polarographic rate. To effect a fast rate of polarization, a 100 ohm one-turn precision potentiometer, whose contact was rotated by a synchronous 1 r.p.m. clock motor, was used as a slidewire. The current in the cell was determined by measuring the potential drop across a precision resistance, connected in series with the electrolysis cell, with a Leeds and Northrup Speedomax recording potentiometer having a full-scale sensitivity of 2.5 mv, a pen with full-scale travel time of 1.2 sec, and a chart speed of ten inches per minute.

In a polarographic determination, the initial potential was adjusted to −0.2 v *vs.* the saturated calomel electrode (S.C.E.) and a polarogram made over the range −0.2 to −1.0 v *vs.* S.C.E. The diffusion current was measured by extrapolating the diffusion plateau to the halfwave potential, measuring the height and subtracting any residual current.

In the coulometric determination use was made of the two interchangeable circuits described previously[8] which permitted the deposition to be carried out at any potential without regard for the potential range covered in the dissolution cycle.

The deposition of lead was effected at a potential of 1.0 v *vs.* S.C.E. The cell was then quickly changed to the slidewire circuit, and the potential scanned from -0.7 to -0.2 v *vs.* S.C.E. For the estimation of lead a rate of polarization of 8.3 mv/sec was convenient, since this covered the -0.7 to -0.2 v range in one turn of slidewire. Dissolution span rates as high as 22 mv/sec and as low as 6.7 mv/sec could be obtained without changing the speed of the motor. One should be careful not to let the potential on the electrode become more positive than about 0.0 v in 0.1M chloride, because a large dissolution current of mercury will be obtained. The amount of current that flowed during this stripping cycle was recorded. From the area of the dissolution curve, estimated either by cutting out the trace with scissors and weighing the paper or by counting the small squares of the chart paper, one could calculate the number of microcoulombs required for the dissolution. Appropriate blanks were always recorded and subtracted from the total current.

For the coulometric determinations on solutions from $5 \cdot 10^{-5} M$ to $1 \cdot 10^{-7} M$ a nominal plating time of 300 sec was employed. However, the actual time of deposition was nearly 30 sec longer since some deposition took place during much of the dissolution cycle. For this reason one would expect a slightly smaller dissolution trace at the higher rate of stripping, since the plating time during the dissolution would be less. Thus, in order to assure a constant plating time, the rate of dissolution and the potential from which the dissolution started were always constant, except where otherwise noted in the text.

REAGENTS AND SOLUTIONS

Approximately $1 \cdot 10^{-3} M$ stock solutions of cadmium, and lead chlorides were made by dissolving the required weight of chemical in a supporting electrolyte of 0.1M reagent grade potassium chloride and distilled water of 400,000 ohms specific resistance. Thallium and copper solutions were similarly prepared from the purest obtainable nitrate salts. The exact concentrations of the various solutions were: lead, $1.01 \cdot 10^{-3} M$; cadmium, $1.05 \cdot 10^{-3} M$; thallium, $1.00 \cdot 10^{-3} M$ copper, $1.10 \cdot 10^{-3} M$. Volumetric dilutions were made with 0.1M potassium chloride to $5 \cdot 10^{-5}$ and $1 \cdot 10^{-6} M$.

For nearly all of the solutions which were to be used in the coulometric calibration runs, the supporting electrolyte was prepared from reagent grade potassium chloride which had been recrystallized from distilled water, and then dissolved in deionized water which had been prepared by passing distilled water through a 70 cm column containing a mixture of IR-120 and IRA-400 ion exchange resins (ROHM AND HAAS). The deionized water had a specific resistance of $1\text{-}2.5 \cdot 10^6$ ohms. For a few studies on $10^{-8}M$ lead solutions a supporting electrolyte prepared from deionized water and reagent grade potassium nitrate, which had been recrystallized four times, was used.

TABLE I

COMPARISON OF WAVE HEIGHTS OBTAINED WITH THE DROPPING MERCURY ELECTRODE AND STATIONARY MERCURY ELECTRODE IN QUIET AND STIRRED MILLIMOLAR SOLUTIONS

Electrode	Ion in 0.1*M* KCl	Wave height (μA)
D.M.E.[a]	Pb(II)	9.52
S.M.E. (Q)	,,	2.88
S.M.E. (S)	,,	18.15
D.M.E.	Tl(I)	5.75
S.M.E. (Q)	,,	2.06
S.M.E. (S)	,,	12.14
D.M.E.	Cd(II)	9.88
S.M.E. (Q)	,,	2.75
S.M.E. (S)	,,	18.65

a. — m 2/3 t 1/6 in 0.1*M* potassium chloride at 24° C is 2.22 at the potential of the saturated calomel electrode.
Q. — quiet solution S. — stirred solution

RESULTS

Polarographic. It can be seen from Table I that the use of the stationary mercury electrode in a stirred solution resulted in a two-fold increase in current over a typical D.M.E. that was used, but, more important, a six-fold increase over the same stationary electrode in a quiet solution. Cadmium and thallium solutions gave similar results. The small fluctuations on the limiting current plateaus made exact determination of the currents somewhat difficult. However, the standard deviation of seven replicates was 3.1% at $1 \cdot 10^{-3}M$. As the dilution was increased, no large change in reproducibility was noted. However, the contribution of the residual current was significantly increased at the high dilution and probably accounts for the non-linearity of the results shown in Table II. At the sensitivity necessary for measurement of the $5 \cdot 10^{-6}M$ solution the reproducibility of the blank was ±5% while fluctuations of the total current were ±15.9%. Therefore the polarographic detection limit was about $1 \cdot 10^{-6}M$.

References p. 585.

TABLE II

CALIBRATION DATA FOR THE POLAROGRAPHIC DETERMINATION OF LEAD

Run No.	Pb^{+2} conc. (M)[a]	Limiting current (inches)[b]	Sensitivity (μA/inch)	id/C (mA/M)
1	$1.01 \cdot 10^{-3}$	5.29	3.40	17.8
2	$1.01 \cdot 10^{-4}$	5.10	0.340	17.2
3	$1.01 \cdot 10^{-5}$	5.81	0.0416	24.0
4	$5.05 \cdot 10^{-6}$	2.86	0.0416	23.6

[a] — by dilution of stock $1.01 \cdot 10^{-3} M$

[b] — average value of duplicate run corrected for blank.

Increasing the polarization rate at which polarograms were made was found to have little effect upon the limiting current, until a rate of 17 mv/sec was reached. Polarograms of lead at this rate of polarization showed rather pronounced maxima, similar to that found at the stationary electrode in unstirred solutions at slower rates of polarization. The small charging current produced by the rapid rate of polarization was easily compensated for by the subtraction of an appropriate blank.

Coulometric. It was found that when working near the maximum sensitivity of the instrument a minimum of approximately one microcoulomb of dissolution current was required to obtain maximum precision. Thus, at $1 \cdot 10^{-5} M$, where the polarographic current was 0.24 μA, a plating time of 4 sec would be sufficient for a coulometric determination; at $1 \cdot 10^{-7} M$, 400 sec. Actually a nominal plating time of 300 sec produced nearly 1 microcoulomb at the $1 \cdot 10^{-7} M$ concentration because of additional plating during part of the dissolution cycle.

A series of solutions of different concentrations were analyzed coulometrically and are given in Table III. The range of $2.5 \cdot 10^{-6}$ to $5 \cdot 10^{-5}$ showed an accumulated standard deviation of 4.7%, which is close to the standard deviation of 3.5% for replicates from aliquots of a single solution. The logarithmic plot, Fig. 2, of the combined coulometric and polarographic data shows close agreement between the two methods. The coulometric deposition currents were obtained by dividing the area of the trace (μA-sec), by the plating time (300 sec) with no attempt to compensate for the additional plating which took place during the dissolution cycle. Differences between Runs 1-5 and 6-10 may in part be due to temperature, but were probably due primarily to an inadvertent change in the position of the electrode. This suspicion was confirmed by the last five runs, (indicated by primes) which were run later and show the expected continuity.

References p. 585.

TABLE III

CALIBRATION DATA FOR THE COULOMETRIC DETERMINATION OF LEAD

Run No.	Pb^{+2} conc. × 10^6 $(M)^a$	Area $(inch^2)^b$	Sensitivity (μA-sec) inch²	id/c $(mA/M)^c$
1	2.53	4.68	3.57	22.16
2	5.1	4.29	7.15	20.30
3	7.6	6.50	7.15	20.40
4	10.1	4.20	14.30	19.80
5	51.0	8.63	35.74	20.40
6	0.101	1.93	0.250	15.9
7	0.202	4.70	0.250	19.4
8	0.51	4.61	0.511	15.5
9	0.71	6.30	0.511	15.2
10	1.01	6.00	0.746	14.8
8′	0.51	4.87	0.746	18.6
9	0.71	5.79	0.746	19.5
10′	1.01	7.95	0.746	19.6
1′	2.53	5.06	2.86	19.1
2′	5.1	10.20	2.86	19.5

a — by dilution of stock $1.01 \cdot 10^{-3} M$
b — average value of duplicate runs corrected for blank.
c — coulometric current divided by 300 second plating time.

To test briefly the interference by other amalgam-forming elements the deposition of lead in the presence of thallium and cadmium was briefly studied. Thallium which has a halfwave potential of −0.46 v *vs.* S.C.E. in $0.1 M$ potassium chloride was expected to give a dissolution trace overlapping that of lead, whose halfwave potential in the same medium is −0.40 v *vs.* S.C.E.[7]. Note in Fig. 3 that the presence of thallium can be detected in the combined dissolution trace when both lead and thallium are present in the same concentration. However, quantitative results for either element cannot be obtained under such conditions. In the case of cadmium, whose halfwave potential is −0.60 v *vs.* S.C.E. no interference with the lead peak was noted when both were $1 \cdot 10^{-6} M$. At the 8.3 mv/sec rate of stripping both the cadmium and lead traces were well resolved and nearly equal in area, the cadmium trace being slightly smaller primarily as a result of the shorter time of plating during the dissolution cycle.

Since the coulometric method has inherently high sensitivity, the feasibility of making determinations at $1.10^{-8} M$ was explored. One can calculate that the total deposition of 100 ml of a $1 \cdot 10^{-8} M$ lead solution would result in a dissolution trace of 193 microcoulombs. Consequently the coulometric deposition

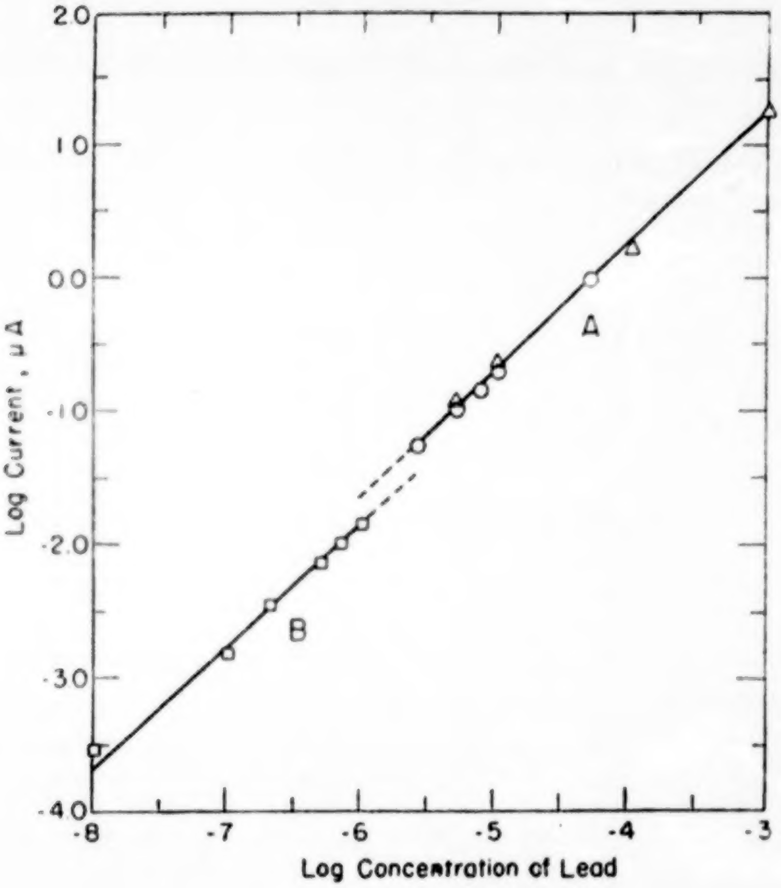

Fig. 2. Two sets of calibration data.
A. Polarographic (△) and coulometric (O) data.
B. Coulometric data after a change in electrode position.

requirement of one microcoulomb would not result in appreciable depletion of the solution.

A rather high blank, indicating the presence of lead, cadmium and possibly copper, was obtained with 0.1*M* recrystallized potassium chloride, so a brief investigation was made of the blank using different reagents and different methods of purifying the water. The curves in Fig. 4 indicated a large difference between deionized water and distilled water for the dissolution area of an element only slightly less noble than mercury. The maximum of this unknown dissolution peak was –0.09 v *vs.* S.C.E. in 0.1*M* potassium chloride and +0.03 v *vs.* S.C.E. in 0.1*M* potassium nitrate. While these potential values do not correspond exactly[7] with those found for the halfwave potential of copper at the dropping mercury electrode, copper was suspected to be the cause. The addition of sufficient copper to the solution of 0.1*M* reagent grade potassium chloride in distilled water, to produce a copper concentration of $1 \cdot 10^{-6}M$ doubled the area of the unknown trace. Thus, if the contaminant were copper, its original concentration was about $1 \cdot 10^{-6}M$. A similar solution of potassium chloride in deionized water showed an amount equivalent to $1 \cdot 10^{-7}M$.

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To ascertain if all of the contaminants could be reduced to a negligible amount, a pre-electrolysis of the supporting electrolyte was made using a large mercury pool held at a potential of −1.0 v *vs.* S.C.E. After two hours mercury was drained from the cell while still under a potential of −1.0 v. Then a coulometric deposition of 3000 sec was made with a mercury-plated platinum electrode. The resulting dissolution curve was completely blank, indicating quantitative removal of the contaminants to less than $10^{-8}M$.

When blank runs of 3000 sec duration were made on solutions of potassium nitrate, which had been recrystallized four times and then dissolved in deionized water, much smaller amounts of lead and other impurities were found than in $0.1M$ potassium chloride. Because pre-electrolysis was not required in order to

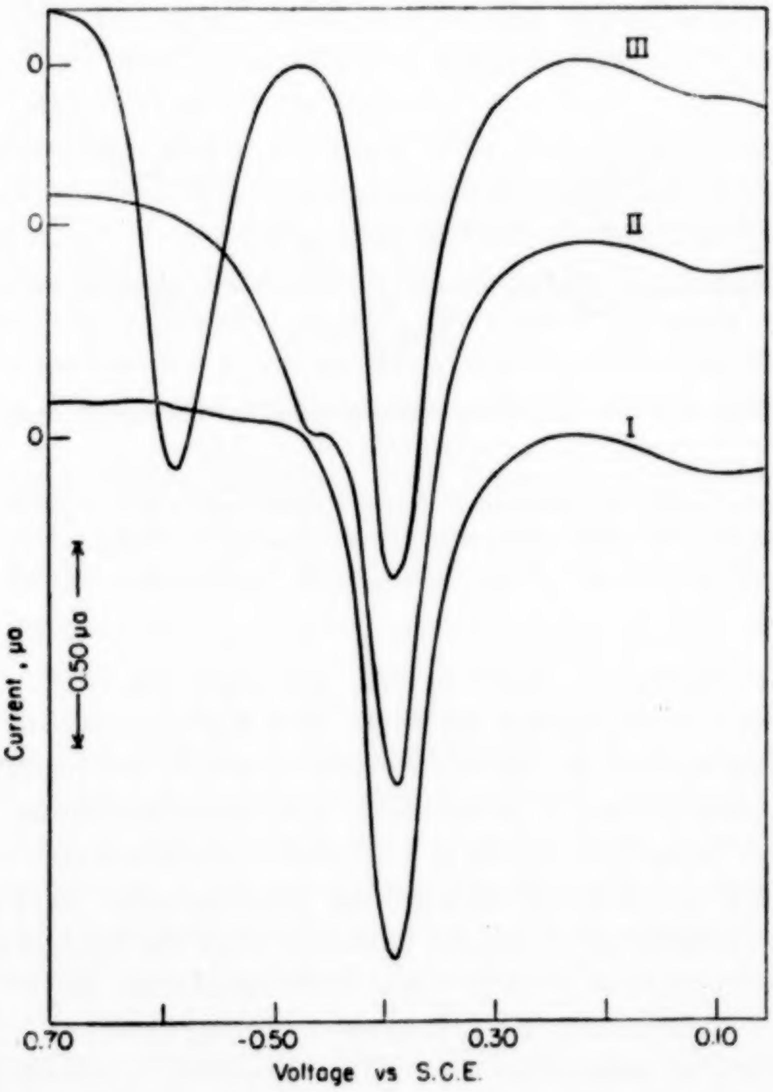

Fig. 3. Effects on the coulometric dissolution curves for lead of adding cadmium and thallium. Supporting electrolyte — $0.1M$ potassium chloride.
I. Millimolar lead.
II. Millimolar thallium and millimolar lead.
III. Millimolar cadmium and millimolar lead.

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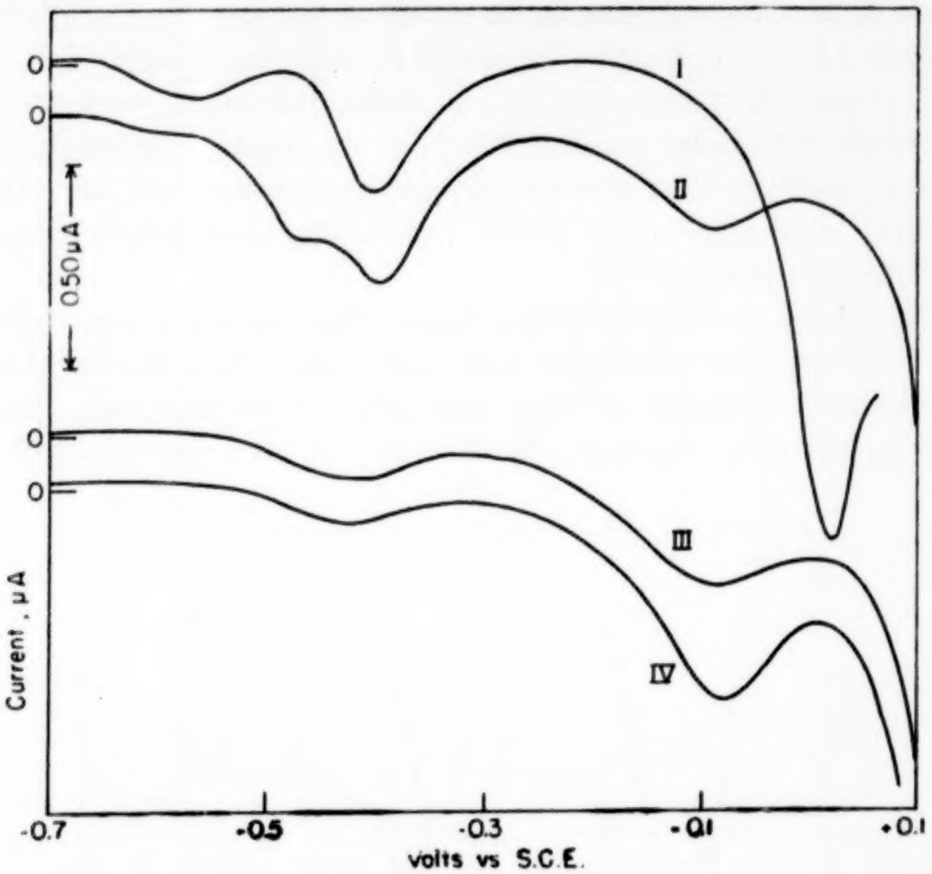

Fig. 4. Coulometric blanks showing impurities in the solutions of background electrolytes.
I. $0.1M$ potassium nitrate prepared from deionized water; 3000 sec electrolysis.
II. $0.1M$ potassium chloride prepared from deionized water; 3000 sec electrolysis.
III. $0.1M$ potassium chloride prepared from distilled water; 300 sec electrolysis.
IV. Same as III but with $10^{-6}M$ cupric ion added.

work with nitrate solutions, most of the attempts to work with a $1 \cdot 10^{-8}M$ solution of lead were made in this medium. In a typical run, the blank obtained for $0.1M$ potassium nitrate in dionized water was 0.82 microcoulombs; the total dissolution area, after adding $1 \cdot 10^{-8}M$ lead, 1.73 microcoulombs. The deposition current calculated from this result is 303 micromicroamperes, while a value of 180 micromicroamperes was calculated from polarographic data at higher concentrations. These fragmentary results indicated that the method could be extended to the determination of lead at these concentrations, but that an empirical calibration curve would be required. However, plating times of this length permit significant amounts of impurities to diffuse from the concentrated electrolyte in the salt bridge. An indication of this was the significantly higher results obtained for successive runs on the same solution. Hence, appropriate steps must be taken for any quantitative work at this level of concentration.

DISCUSSION

Early in the investigation it was observed that when the electrode was stored in either distilled water or air, erratic results were sometimes obtained. The reason for the erratic behavior could not be found, but it was believed to be a leak in the platinum-glass seal, a loss of mercury from the electrode (thereby exposing bare platinum), or the formation of an oxide layer on the electrode. To prepare a better platinum-glass seal, lead glass was substituted for ordinary soft glass. These seals were so much more reliable that no electrodes have as yet been lost due to cracking of the seal. The possible loss of mercury was eliminated by storing the electrode at a potential of –0.3 v *vs.* the S.C.E. in a solution of 0.1 potassium chloride. During the long periods of storage, the electrode gathered some impurities from the electrolyte, but these could be removed before using the electrode by holding it for a short time at a potential only slightly more negative than the potential for the dissolution of mercury.

Although the position of the electrode with respect to the stirring tube was held constant during most of the measurements reported here, it was of interest to determine the effect on the deposition current of changing the position of the electrode within the rotating tube. When the electrode was moved from the center of the stirring tube to a position as near the edge as possible, a +46% increase in current was observed for a $5.0 \cdot 10^{-5} M$ solution. The resulting current was nearly ten times that obtained polarographically in an unstirred solution and, hence, compares more favorably with the increase obtained by rotating an electrode. However, when the electrode was near the center of the tube, a comparatively small error resulted if the electrode were moved. A variation of this type has been shown in the coulometric results of Fig. 2, where an attempt was made to restore the electrode to its original position after it had been accidentally moved.

Preliminary coulometric experiments using a supporting electrolyte of 0.1*M* potassium chloride and 0.016*M* nitric acid showed that the amounts of lead and cadmium deposited were functions of the deposition potential, even when that potential was several tenths of a volt more negative than the halfwave potential. In 0.1*M* potassium nitrate, 0.1*M* potassium chloride, or a mixture of 0.05 potassium chloride and 0.05 potassium nitrate, a change of the deposition potential from –1.0 v to –0.7 v produced an average decrease of 14%.

This decrease was verified polarographically by observing that the addition of nitric acid, hydrochloric acid or perchloric acid produced limiting currents with decided slopes for lead at the mercury-electrode in stirred solutions. In most of the polarograms one could see what appeared to be a second drawn-out wave extending from about –0.6 to –1.0 v. The addition of more acid up to 0.16*M* produced little additional effect. Typical results upon polarograms made in quiet and in stirred solutions are illustrated in Fig. 4. By using a 6-10 sec recorder

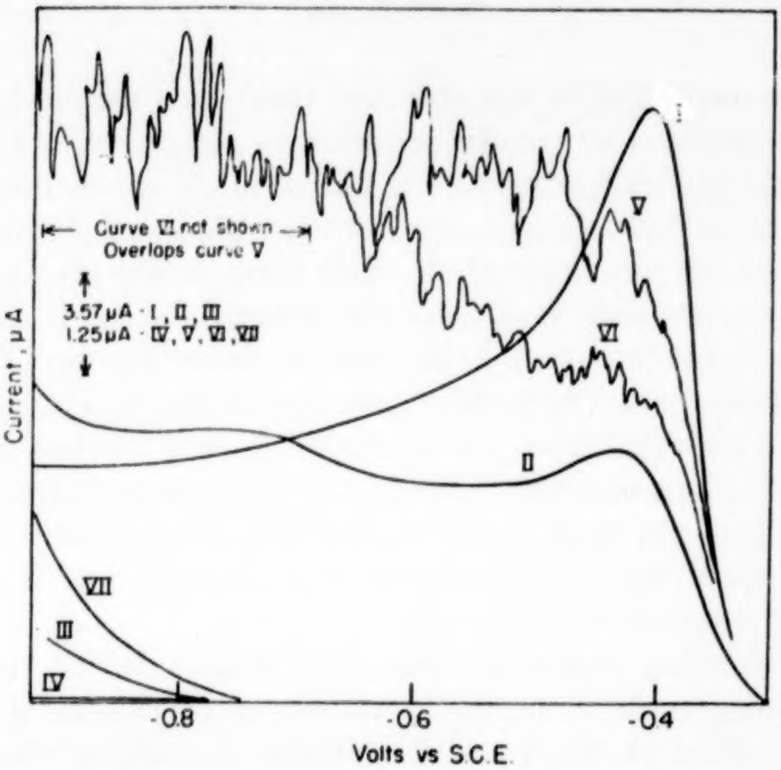

Fig. 5. Effect of added acid on the polarographic waves of millimolar lead in 0.1 M potassium chloride.

I. Unstirred solution; no acid present.
II. Unstirred solution; 0.016 M nitric acid present.
III. Blank run for (II).
IV. Blank for unstirred and stirred solutions in the absence of acid.
V. Stirred solution; no acid present.
VI. Stirred solution; 0.016 M nitric acid present.
VII. Blank run for (VI).

(Sargent Model XXI polarograph) instead of 1.2 sec, the extreme variability of the limiting current for stirred solutions is reduced to a line with quite regular oscillations having a maximum variation of ±4% from the average. One can determine the average current for such a polarogram with the same ease as that obtained with a dropping mercury electrode. Note that the addition of acid flattened the maximum obtained in a quiet solution as well as affecting the results in stirred solutions. If the second wave observed in stirred solutions is real, some interesting theoretical questions arise since lead in a chloride medium is oscillographically reversible[4].

Cadmium, like lead, showed a limiting current with a slope but it was linear without any sign of a possible second wave. Thallium was also tested but no effect from added acid was observed.

ACKNOWLEDGEMENT

The authors are indebted to the Atomic Energy Commission for partial support.

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SUMMARY

A stationary mercury-plated platinum electrode in a rapidly stirred solution has been applied to the polarographic and coulometric determination of trace amounts of lead(II). Once the equipment has been assembled and calibrated, analyses of micromolar solutions can be completed in less than ten minutes each with a precision of about 5%. The method avoids the lengthy preparation of reagent solutions and the tedious extractions encountered in the competitive dithizone procedure. Furthermore, it can handle more dilute solutions than those usually analysed by dithizone, (*i.e.* as low as $10^{-8}M$). The method should be equally applicable to a number of other heavy metal ions.

RÉSUMÉ

Une électrode fixe, spéciale („mercury-plated platinum electrode"), plongeant dans une solution agitée rapidement, a été appliquée au dosage polarographique et coulométrique de traces de plomb(II). Lorsque l'appareillage est monté et calibré, le dosage d'une solution micromolaire peut être effectué en moins de 10 minutes avec une précision d'environ 5%. Cette méthode permet d'éviter les longues préparations des solutions de réactif et les nombreuses extractions nécessaires pour le dosage à la dithizone. D'autre part, ce procédé permet de travailler avec des solutions plus diluées encore que celles généralement utilisées par le procédé à la dithizone; (par exemple: $10^{-8}M$). Cette méthode est également applicable à un certain nombre d'autres métaux lourds.

ZUSAMMENFASSUNG

Es wird eine spezielle feste Elektrode („mercury-plated platinum electrode"), die in eine stark umgerührte Lösung taucht, für die polarographische und coulometrische Bestimmung von Blei(II) in Spuren verwendet. Wenn der Apparat montiert und kalibriert ist, kann die Bestimmung einer mikromolaren Lösung in weniger als 10 Minuten ausgeführt werden mit einer Präzision von ungefähr 5%. Durch die Anwendung dieser Methode werden die langwierigen Präparationen der Reaktionslösungen sowie die zahlreichen für die Bestimmung mit Dithizon notwendigen Extraktionen vermieden. Zudem kann bei dieser Methode mit Lösungen grösserer Verdünnung gearbeitet werden als dies im allgemeinen für die Dithizonmethode möglich ist (z.B. $10^{-8}M$). Dieses Verfahren ist auch für eine bestimmte Anzahl weiterer Schwermetalle anwendbar.

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POLAROGRAPHIC DETERMINATION OF URANIUM IN ORES IN ASCORBIC ACID SUPPORTING ELECTROLYTE

by

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INTRODUCTION

In a recent publication, ŠUŠIĆ[1] proposed *l*-ascorbic acid as supporting electrolyte for the polarographic determination of uranium in the presence of many other cations. Uranyl salts in 0.5 *M* ascorbic acid solutions at pH 3.5-4.0 give a well-defined wave; the half-wave potential is about — 0.36 v *vs*. S.C.E. The diffusion current is proportional to the uranium concentration. At higher pH the wave is shifted to a more negative value, indicating that the yellow-coloured soluble compound, formed from uranyl ion and ascorbic acid, should be partially dissociated in acidic solutions.

The polarographic properties of the ascorbic acid as supporting electrolyte are based on its reduction- and complexing-power. Ascorbic acid, for example, reduces Fe(III)—, V(V)—, Mo(VI)—, Cr(VI)—, etc, ions, and so they do not interfere in the polarographic determination of uranium. With titanium a red-coloured, soluble complex is formed. Its half-wave potential is more negative than that of uranyl ion and the two waves are well separated. The cupric wave precedes that of uranium by about 0.30 v and so copper does not interfere if not present in excessive quantity.

In this work we used ascorbic acid as supporting electrolyte in the polarographic determination of uranium in ores. The determinations were carried out immediately after attacking the samples, without any previous chemical separation. The results of analyses of several ores are reported and compared with results obtained by other analytical methods.

EXPERIMENTAL

Four ores with different uranium content were analysed: one epidote and three schists. The uranium concentrations were in the range 0.01-0.1%. All samples were rich in SiO_2 (50-80%), with Fe_2O_3, Al_2O_3 and CaO from 1-30%. Between minor components we found Ti, V, Cu, but no complete analysis of traces was performed. The schists were rich in organic matter and so were roasted before analysis. Samples of 1-2 g of finely ground ore were taken and attacked with concentrated HNO_3 and 40% HF, but, of course, any other convenient attack could be applied. After dissolving, a little sulfuric acid was added to the nitrate solution and evaporated to dryness. The residue was taken up with distilled water and crystalline ascorbic acid was added (to make the final solution 0.5 *M*). Then, aqueous ammonia was added dropwise and the pH adjusted between 3.6-4.0. (In routine analysis a good pH-paper is sufficient for the pH control. However, in some cases a finer pH adjustment may be desirable). Finally, the solution was transfered to a 25 or 50 ml volumetric flask, 0.2-0.4 ml 1% gelatine solution was added and the solution made up to volume.

For polarographic determinations 5 and 10 ml aliquots were taken. Before running the polarograms, pure nitrogen was bubbled through the solution for 15 minutes. The method of standard addition was utilized and in order to prevent changes in pH caused by the addition, only 0.05 or 0.1 ml of a standard UO_2SO_4 solution was added, using a precise syringe-type micropipette. Polarograms were started at —0.05 and —0.1 v *vs.* S.C.E. The uranium waves were recorded from —0.35 to —0.45 v.

Apparatus and reagents. A pen-recording polarograph made by Messrs. Radiometer, Copenhagen, served for all determinations. The reference electrode was a saturated calomel electrode (S.C.E.).

All solutions used were prepared from Analytical Grade reagents. Crystalline 1-ascorbic acid was obtained from E. Merck, Darmstadt.

RESULTS AND DISCUSSION

In the first column of Table I, results of polarographic determinations of four ores are tabulated. Each result represents the mean value computed from 4-5 duplicate analyses, *i.e.* the mean value of 8-10 measurements. Also the standard deviations for a single measurement (S.D.) are given. The same is true for the results obtained by other analytical methods given in Table I.

TABLE I

Method: Ores:	polarographic U, ppm	polarographic (S.D.) ppm	colorimetric U, ppm	colorimetric (S.D.) ppm	fluorimetric U, ppm	fluorimetric (S.D.) ppm	radiochemical U, ppm	radiochemical (S.D.) ppm
Epidote	1006	±28			1020	±60	970	—
Schist I.	345	25	338	±26	346	28	325	—
Schist II.	300	23	292	27	294	14		
Schist III.	194	16	191	20	196	16		

As seen from Table I, our results are compared with colorimetric, fluorimetric and radiochemical determinations of uranium. The agreement between the mean values is excellent. Now, a few words concerning the three methods mentioned. For colorimetric determinations the well-known thiocyanate method was utilized, combined with a previous ether-extraction of uranyl nitrate[2]. The fluorimetric method is described in more detail elsewhere[3, 4]. Two radiochemical methods were applied. The first ore (Epidote) with higher uranium content was suitable for radiochemical analysis using β-and γ-counters, as described by THOMMERET[5]. For the second ore (Schist I) this method is not sensitive enough and therefore a radioactivation analysis[6] was carried out.

Under the conditions mentioned before, we found that Te-, Tl- and Pb-polarographic waves coalesce with that of uranium. Further, large amounts of Sb mask the uranium wave. Practically, only lead is common in uranium ores, but its interference could be eliminated in many cases if the determination is carried out at lower pH. Interferences due to Te, Tl and Pb are easily eliminated as described in a previous paper[1].

The polarographic method using ascorbic acid supporting electrolyte could be very useful in routine work, as no chemical separations are required. The method is suitable for ore-samples with a uranium content above 0.01%. In the concentration range 0.01-0.05% the relative error of a single determination is 5-9%; above 0.05% U the precision is much greater.

ACKNOWLEDGEMENTS

Our thanks are due to Professor P. SAVIĆ for his interest and the support he gave during the work. We are indebted to Miss D. MILOŠEVIĆ who helped us in preparing the ore-samples and to D. CVETIŠANIN, Miss N. BELEGIŠANIN AND V. JOVANOVIĆ for some colorimetric and fluorimetric analyses.

SUMMARY

A polarographic determination of uranium in ores using 0.5 *M* *l*-ascorbic acid as supporting electrolyte is described. Four different ores were analysed and the results compared with those obtained by other analytical methods. No previous chemical separations were necessary. The method is simple, rapid and seems to be suitable for routine analyses of samples with a uranium content above 0.01%. In the concentration range 0.01—0.05%, the relative error of determination is 9—5%; above 0.05% U the precision is much greater. Te, Tl and Pb interfere in this method under the conditions described (pH 3.5—4.0), but the interference due to lead is eliminated in many cases by lowering the pH of the solution.

RÉSUMÉ

Une méthode polarographique est décrite pour le dosage de l'uranium. On utilise l'acide ascorbique 0.5*M* comme solution de base. Quatre minerais différents ont été analysés et les résultats ont été comparés avec ceux obtenus par d'autres métho-

des. Ce procédé est simple et rapide. Il convient très bien pour des dosages en série d'échantillons contenant plus de 0.01 % d'uranium. Pour des teneurs comprises entre 0.01 et 0.05 %, l'erreur relative est de 9 à 5 %; pour des teneurs supérieures à 0.05 % la précision est plus grande. Certains éléments, notamment Te, Tl et Pb gênent, dans les conditions décrites (pH 3.5 à 4.0), mais la perturbation due au plomb peut être éliminée dans la plupart des cas en abaissant le pH de la solution.

ZUSAMMENFASSUNG

Eine polarographische Bestimmungsmethode für Uran in Erzen ist beschrieben. Als Grundelektrolyt diente eine 0.5*M* Lösung von Askorbinsäure. In vier verschiedenen Erzen wurde Uran bestimmt und die erhaltenen Resultate mit denjenigen anderer analytischen Methoden verglichen. Preliminäre chemische Trennungen wurden nicht durchgeführt, da sie sich als unnötig erwiesen. Die beschriebene Methode ist einfach, schnell und scheint fur Betriebsanalysen günstig zu sein. Die Methode ist für Erze mit einer Urankonzentration oberhalb 0.01 % anwendbar. Für Urangehalte zwischen 0.01—0.05% beträgt der relative Bestimmungsfehler 9—5 %; oberhalb 0.05% ist die Präzision der Methode jedoch viel grösser. Te, Tl und Pb stören bei dieser Bestimmung. Die Störung durch Blei kann in vielen Fällen durch einfache Erniedrigung des pH der Lösung eliminiert werden.

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DÉTERMINATION POLAROGRAPHIQUE INDIRECTE DES SULFATES

II. APPLICATION À L'ANALYSE DES EAUX

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Dans un travail précédent[1], nous avons étudié le système SO_4^{-2}-Pb^{+2}/$PbSO_4$ en vue de son utilisation pour la détermination polarographique indirecte des sulfates. Une solution renfermant un sulfate, dans des conditions bien définies de force ionique et de température, agitée avec du sulfate de plomb, conduit à un état d'équilibre capable d'être caractérisé par la concentration de plomb dans la solution finale. Les essais de détermination indirecte des sulfates par la mesure polarographique du plomb, ont donné des résultats très précis.

Pour travailler avec des solutions de concentration saline pratiquement constante on pourrait ajouter un électrolyte en quantité telle que la concentration saline résultante serait peu affectée par les variations de concentrations des solutions originales. Mais des études postérieures nous ont conduit à une possibilité plus élégante, plus pratique et capable d'étendre les applications de la méthode. On procède comme suit: 1. La solution renfermant le sulfate est passée à travers une colonne contenant un échangeur de cations. La solution est ainsi libérée des cations présents. 2. Les acides, s'ils sont volatils, sont éliminés par évaporation à sec, en présence d'un électrolyte, par exemple, le nitrate de potassium, servant de support dans la mesure polarographique. Dans ces conditions, le résidu dissous dans un volume bien déterminé, donnera une solution de concentration parfaitement définie, indépendamment de la composition originale de la solution.

S'il y a dans la solution primitive un anion d'acide non volatil, il est en général possible de le séparer avant d'utiliser l'échangeur de cations.

En suivant le plan général exposé ci-dessus, nous avons mis au point des procédés spéciaux pour la détermination des sulfates: 1. dans les eaux; 2. dans les acides et dans les sels; et 3. de soufre dans les fers et aciers. Le présent travail traite seulement du premier cas.

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PARTIE EXPÉRIMENTALE

Réactifs.

a) Nitrate de potassium $0.5M$.

b) Acide sulfurique $0.005M$. La solution est préparée à partir d'une solution $0.1M$ par dilution convenable.

c) Acide nitrique $0.05M$.

d) Gélatine à 0.1%.

e) Sulfate de plomb[1].

f) Amberlite IR-120.

Appareils

a) Polarographe du type Heyrovsky, de la firme allemande Leybold, avec capillaire du même fabricant; temps de formation de goutte égal à 1.6 secondes; hauteur de la colonne de mercure: 60 cm.

b) Cellule polarographique: type Heyrovsky. Contrôle de la température: ± 0.5° C.

c) Appareil de TOMPKINS, KHYM ET COHN[2].

Courbe étalon. Introduire avec la pipette, dans des capsules en porcelaine (de 11 cm de diamètre) 20 ml de nitrate de potassium $0.5M$. Ajouter, respectivement, 0, 6.00, 12.00, 24.00 et 30.00 ml d'acide sulfurique $0.005M$. Evaporer à sec, au bain-marie électrique. Dissoudre le résidu dans le minimum d'eau, évaporer et porter à l'étuve à 120° C pendant 30 minutes; dans cette opération, l'acide sulfurique déplace une quantité équivalente d'acide nitrique. Extraire avec de l'eau et transvaser dans une fiole jaugée de 100 ml. Additionner 10 ml d'acide nitrique $0.05M$ et 10 ml de solution de gélatine à 0.1% et compléter avec de l'eau. Introduire environ 20 ml dans la cellule polarographique, ajouter 0.1 g de sulfate de plomb et faire passer un courant d'azote pendant 30 minutes. Polarographier sous atmosphère inerte avec une sensibilité de $^1/_{30}$.

Détermination du sulfate dans les eaux. Passer une quantité suffisante d'eau à travers une colonne de TOMPKINS, KHYM ET COHN, chargée avec de l'Amberlite IR-120, à la vitesse de 0.01 à 0.05 ml par ml de l'échangeur par minute. Transvaser avec la pipette 50 ml dans une capsule de 11 cm de diamètre, et ajouter 5 ml de nitrate de potassium $0.5M$. Evaporer, à sec, au bain-marie électrique. Ajouter le minimum d'eau pour dissoudre le résidu, évaporer et chauffer à l'étuve à 120° C, pendant 30 minutes. Dissoudre dans 25 ml d'acide nitrique $0.005M$, contenant 0.01% de gélatine. Transvaser dans la cellule polarographique et ajouter environ 0.1 g de sulfate de plomb. Envoyer de l'azote à travers la solution pendant 30 minutes. Polarographier avec une sensibilité de $^1/_{30}$.

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RÉSULTATS

La Fig. 1 (courbe A) représente une courbe étalon. En abscisses sont données les concentrations de sulfate en p.p.m. pour le procédé tel qu'il a été décrit ci-dessus, et également en mole/litre dans la solution finale.

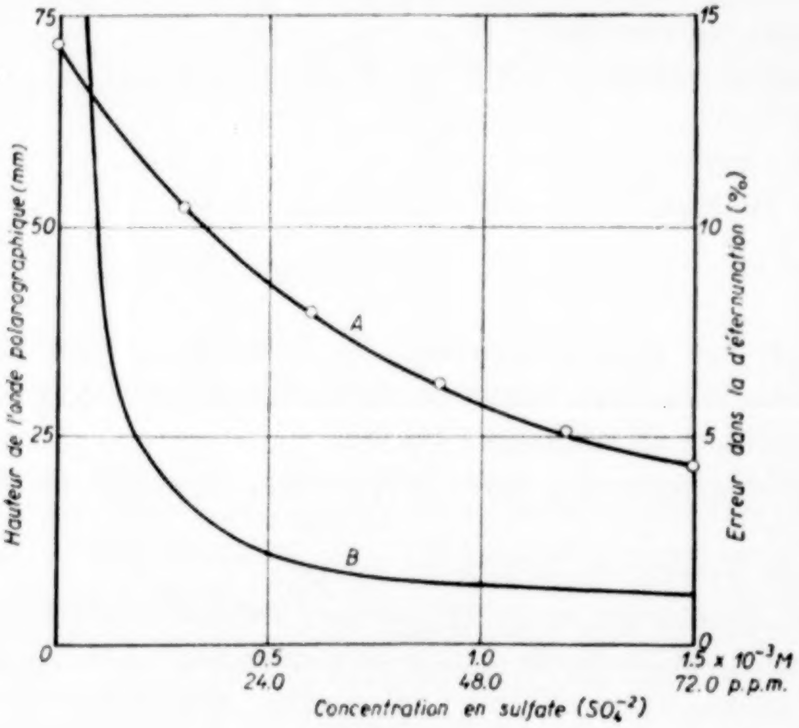

Fig. 1

La méthode polarographique de détermination indirecte de sulfate a été appliquée à l'analyse d'un échantillon d'eau traitée, de la ville de P. Alegre, renfermant 26.7 p.p.m. de SO_4^{-2}. Les résultats trouvés sont:

Essais	Résultats trouvés (p.p.m.)	Erreur (%)
1	27.3	2.2
2	27.1	1.6
3	26.8	0.5
4	26.2	1.7

CONCLUSION

La méthode polarographique de détermination indirecte des sulfates est applicable à l'analyse des eaux. Notre expérience indique que la mesure polarographique du plomb peut être faite avec une précision de 1%. La courbe B, Fig. 1, représente l'erreur relative dans la détermination du sulfate en supposant une erreur de 1% dans la mesure polarographique du plomb. Les meilleures conditions de travail sont celles qui correspondent aux concentrations de 0.5 à $1.5 \cdot 10^{-3} M$

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de SO_4^{-2}. Pour les essais ci-dessus, la solution finale était $0.556 \cdot 10^{-3} M$ en SO_4^{-2}. Si c'est nécessaire, le procédé recommandé peut être modifié pour que la concentration en sulfate dans la solution finale reste dans l'échelle mentionnée.

RÉSUMÉ

Dans le présent travail, l'auteur applique à l'analyse des eaux, la méthode polarographique de détermination indirecte du sulfate, étudiée précédemment,. Les déterminations peuvent être réalisées avec une erreur inférieure à 3%.

SUMMARY

In this paper the author applies the polarographic method of indirect sulfate determination, studied by him in an early work, to water analysis. The determinations can be made with an error under 3%.

ZUSAMMENFASSUNG

In der vorliegenden Arbeit wendet der Verfasser die von ihm in einer früheren Veröffentlichung dargelegte indirekte Sulfatbestimmung auf polarographischem Wege, auf die Wasseranalyse an und findet, dass der dabei begangene Fehler geringer als 3% sein kann.

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BOOK REVIEWS

Substances naturelles de synthèse, collection publiée sous la direction de LÉON VELLUZ, préface de CH. DUFRAISSE. Volume IX, par A. ALLAIS, J. MATHIEU, A. PETIT, P. POIRIER, L. VELLUZ. Un volume de 186 pages et une planche, tableaux. Masson et Cie, Paris 1954. Broché 1.880 fr., cartonné toile 2.280 fr.

La collection poursuit bravement sa route. Ce tome IX est particulièrement riche et présente un intérêt considérable par son chapitre *Méthodes* qui nous fait part de la manière dont on peut introduire l'hydrogène, le carbone, l'oxygène, l'azote, le phosphore et les halogènes marqués dans une molécule en se servant des produits radio-actifs commerciaux en fournissant des exemples de synthèse. Des tableaux fort clairs avec références, indiquent la manière de faire les principaux réactifs isotopiques. Dans le chapitre *Préparations*, on trouve décrite tout au long, la préparation de la testostérone marquée au carbone 14; le corps obtenu peut être très utile pour l'étude du métabolisme des stéroides. Les autres corps préparés se disputent l'actualité biologique; ce sont l'hétéro-auxine, la cystine racémique, l'hydroxylysine, la spermine, la putrescine, la thymine, avec des notes copieuses, non seulement sur ces corps eux-mêmes, mais aussi sur leurs dérivés immédiats. L'ouvrage se termine par une étude des méthodes de dédoublement des racémiques et une liste explicative des agents de dédoublement. La présentation du livre est parfaite; le format, les caractères, les formules, les tableaux ne laissent rien à désirer.

C. DUVAL (Paris)

Ergebnisse der Enzymforschung, R. WEIDENHAGEN, Neuoffstein/Pfalz (HEINZ GIBIAN, Berlin, PETER KARLSON, Tübingen; WOLFGANG LANGENBECK, Rostock; HERMANN MIX, Rostock). Akademische Verlagsgesellschaft, Geest und Portig K.-G., Leipzig, 1954. 314 Seiten, 25 Abbildungen. Preis: DM 25.50.

In der Akademischen Verlagsgesellschaft, Leipzig, ist der 13. Band des Werkes *Ergebnisse der Enzymforschung* erschienen, der dieses Mal drei verschiedenen Forschungsrichtungen gewidmet ist.

Im ersten Aufsatz gibt HEINZ GIBIAN einen erschöpfenden Überblick über die derzeitige Entwicklung der Forschung über das Hyaluronsäure-Hyaluronidase-System. Nach einer eingehenden Darstellung der chemischen und biologischen Wirkungen der Hyaluronidasen gibt der Verfasser eine ausführliche Beschreibung der Test- und Bestimmungsmethoden für dieses Enzym und ferner eine Übersicht aller bisher aufgefundenen Inhibitoren, die, ebenso wie die Hyaluronidase selbst, in letzter Zeit Verwendung zu diagnostischen und therapeutischen Zwecken gefunden haben. Besonders bemerkenswert ist die außerordentlich reichhaltige Zusammenstellung der über dieses sehr interessante Forschungsgebiet bisher erschienenen Literatur.

Im zweiten Abschnitt unternimmt PETER KARLSON den schwierigen Versuch, die biochemische Wirkungsweise der Gene aufzuklären. Nach einer Beschreibung des experimentellen Vorgehens, das die Mutabilität der Gene zur Aufdeckung des Reaktionsweges zu zahlreichen genabhängigen Zellprodukten ausnutzt, untersucht der Verfasser die Einwirkung der Gene auf die Fermentbildung an einigen Beispielen: Zahlreiche Versuche über die Pigmentbildung bei Pflanze und Tier, die Untersuchungen an *Neurospora crassa* über Stoffwechselprodukte, die Erforschung der Bildung von Sexual- und Sterilitätsstoffen bei Pflanzen und die Experimente zur

Genetik einiger spezifischer genabhängiger Zellbestandteile werden in hervorragender Weise geschildert. Mit großem Scharfblick diskutiert schließlich der Verfasser die Versuchsergebnisse im Hinblick auf zukünftige Probleme der biochemischen Genetik.

Der folgende Bericht von HERMANN MIX UND WOLFGANG LANGENBECK über die neuere Entwicklung der organischen Katalysatoren knüpft an einen im Jahre 1933 im Bd. 2 der *Ergebnisse der Enzymforschung* erschienenen Aufsatz über das gleiche Thema an. Die vorliegende Darstellung beschäftigt sich vor allem mit den Beziehungen zwischen den künstlich hergestellten organischen Katalysatoren und den natürlichen Enzymen sowie mit dem Versuch, aus diesen Beziehungen die Konstitution und die Wirkungsweise der Enzyme aufzuklären. Nach einer eingehenden Definition der Enzyme, der Fermentmodelle und der aktiven und aktivierenden Gruppen sowie einer Diskussion der Möglichkeiten zur systematischen Aktivierung organischer Katalysatoren beschreiben die Verfasser die Katalysatorklassen: u.a. die organischen Metallkomplexkatalysatoren und die Covalenzkatalysatoren. Kinetische Betrachtungen, die Feststellung der Regelmäßigkeiten zwischen Molekülbau und Aktivität und eine Abhandlung der stereochemischen Spezifität der Fermentmodelle ergänzen die Darstellung. Hervorzuheben ist die Systematik und Logik, mit der die komplizierten Probleme der Enzymwirkung von der chemischen Seite angegriffen und zum Teil gelöst wurden. Mithin ist auch dieser Band der *Ergebnisse der Enzymforschung*, die heute zu einem unentbehrlichen Bestandteil der chemischen Literatur geworden sind, für den biologisch interessierten Chemiker eine wichtige Ergänzung seiner Bibliothek; aber auch der auf anderen Fachgebieten tätige Chemiker, Biologe oder Physiologe wird ihm mancherlei Anregungen für seine Arbeit entnehmen können.

A. DORNOW (Hannover)

Lehrbuch der Organischen Chemie (in drei Bänden) von F. KLAGES. Walter de Gruyter & Co., Berlin, 1954. Band III, 603 Seiten, 126 Abb., 40 Tab., Ganzl. DM 68.—.

Le troisième volume du Traité de Chimie Organique du Prof. F. KLAGES vient de sortir de presse (cf. *Anal. Chim. Acta*, 7 (1952) 594 et 10 (1954) 296). A notre sens, ce volume a de fortes chances de rester le plus intéressant et le plus utile aussi, parmi les quatre qui formeront le Traité complet.

Consacré à l'étude des bases théoriques de la chimie organique, il présente en effet un caractère d'inédit qu'il est beaucoup plus difficile de trouver dans un ouvrage descriptif et de systématique.

Restées très tardivement à un état quasi embryonnaire, ces bases théoriques se sont considérablement développées depuis quelques années. Même en laissant de côté le calcul mathématique des molécules et d'une manière générale l'aspect quantitatif qui reste encore l'apanage des spécialistes de la mécanique ondulatoire — en réalité plus proches des physiciens que des chimistes au sens classique du mot — le praticien dispose actuellement d'une foule de notions d'ordre qualitatif extrêmement utiles lorsqu'il s'agit de comprendre le mécanisme d'une réaction ou au contraire d'en prévoir plus ou moins la possibilité. Malheureusement ces notions sont souvent dispersées dans une abondante littérature et de ce fait peu accessibles.

Ce sont précisément ces notions théoriques „pratiques", que le Prof. KLAGES a rassemblées, et fondues en un tout ordonné et homogène dans le troisième volume de son Traité.

Nous allons donner maintenant un très bref aperçu de la matière de cet ouvrage:

1. Historique.
2. Méthode physiques en chimie organique (paramètres à propriétés additives, propriétés optiques et électriques, dimensions des molécules, etc.).

3. Liaisons et systèmes de liaisons (liaisons simples et multiples, mésomérie, conjugaison, etc.).
4. Réactions et mécanismes réactionnels (cinétique et thermodynamique. Théorie électronique, propriétés nucléophiles et électrophiles, problèmes typiques, etc.).
5. Tautomérie.
6. Forces intermoléculaires et leurs manifestations.
7. Stéréochimie (divers types d'isomères, isolement des isomères et détermination de leur structure, réactions d'isomérisation, théorie des tensions et inhibition stérique, vraies grandeurs des molécules, modèles, etc.).

G. BARBEZAT (Genève)

Experimental Inorganic Chemistry, by R. E. DODD AND P. L. ROBINSON, Elsevier Publishing Company, Amsterdam, 1954. 424 pages, 162 figures, 35 tables. Prix: $ 6.50 (42*s*).

Le premier chapitre de ce livre donne les techniques de base employées en chimie minérale, en s'appuyant sur des schémas particulièrement clairs et expressifs. C'est ainsi que sont expliquées notamment les techniques de précipitation, cristallisation, filtration, centrifugation, distillation, dessication, sublimation, etc., etc. . .

Le deuxième chapitre est consacré à la manipulation des gaz et à la technique du vide.

Trois chapitres exposent ensuite les méthodes de préparation et de purification des substances minérales des plus communes aux plus rares. Dans chaque cas toutes les constantes physiques connues sont données.

Un dernier chapitre est consacré à ces constantes et à leur détermination.

Enfin suit une liste de références bibliographiques, après laquelle sont encore données les précautions à prendre contre les dangers de la chimie (feu, explosion, toxicité, etc. . .).

Ce livre, dont l'impression est des plus soignées, est destiné aux chercheurs débutants. Il offre certainement le maximum de renseignements sous un volume relativement petit. Ce sera un guide pratique très apprécié des chimistes appelés à travailler dans le domaine de la chimie minérale.

G. PERRET (Genève)

Ausführung qualitativer Analysen, von Prof. Dr. S. WALTER SOUCI, unter Mitwirkung von Prof. Dr. H. THIES und Prof. Dr. FRANZ FISCHLER, 6te ergänzte und verbesserte Aufl. Verlag J. F. Bergmann, München, 1954, 132 Seiten, DM. 6.60

A text-book that reaches its 6th edition since 1932 has amply shown its usefulness in some group of University courses. Indeed it gives an impression of great thoroughness and attendance to minute details. Its most striking feature is that with each reaction careful attention is paid to possible interferences, more than in any other introductory book known to the reviewer. On the other hand it is remarkable that hardly anything has been taken up to show the students that by now there exist newer methods and newer reagents, which have given a completely new aspect to qualitative chemical analysis.

C. J. VAN NIEUWENBURG (Delft)